# INK MANUFACTURE

# INK MANUFACTURE

INCLUDING

## WRITING, COPYING,

## LITHOGRAPHIC, MARKING, STAMPING

AND

## LAUNDRY INKS

BY

SIGMUND LEHNER

TRANSLATED FROM THE GERMAN OF THE FIFTH EDITION

BY

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# PREFACE

In preparing this fifth edition the author, as in the preceding ones, has strictly adhered to the practice of including only such novelties as have been proved useful by his own personal experience. This edition can therefore claim, like those which have preceded it, to contain the whole of the reliable information available at the time of going to press. The old text has also been carefully revised and amended where necessary. In each case where it appeared that such a course would assist an intelligent comprehension of the matter, the recipes are accompanied by a detailed criticism. The author desires to repeat that every recipe in the book has been practically tested by himself, so that he can guarantee good results to every one who will use raw materials of good quality, and follow the recipe exactly. If anything goes wrong the manufacturer must always be sure that he has made no mistake in his operations and that his materials were of good quality before he blames the recipe. It often happens, with dye-extracts particularly, that the materials used would give a bad result with the best of recipes.

The continual increase in the use of the typewriter makes special dyes for the ribbons of those machines

necessary. This book contains recipes for making these dyes, and for dyeing the ribbons, which, in view of the exorbitantly high prices charged for these ribbons, will be an addition to the work greatly appreciated by many of its readers.

The properties of all the raw materials entering into the composition of the recipes are accurately described, so that the reader is provided with a guide to assist him in purchasing them. The author concludes by expressing a hope that all persons skilled in any branch of the ink trade will assist him with any new recipes that have proved valuable in their hands for a new edition, and thanks them heartily in anticipation.

SIGMUND LEHNER.

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# I.

## INTRODUCTION.

Since human progress reached the stage of written communication of ideas, there has been a constant endeavour to simplify writing materials, just as in modern writing we have the tendency to simplify the forms of the symbols, and thus to facilitate the acquisition of the important art of writing.

The Assyrians wrote cuneiform inscriptions on tablets of clay, and the Egyptians chiselled hieroglyphics on granite, or painted them with the brush on the walls of their tombs and temples. The first impulse to the general practice of writing, however, came with the invention of papyrus, which stands in close relationship to paper. That modern writing material derives indeed its name from the word papyrus. Very many papyrus-rolls have come down to us from the ancient Egyptians, and show that a huge number of that race were able to write, especially as the papyri include memoranda of comparatively small importance, such as cookery recipes.

Long after the Chinese and Japanese had learnt the art of writing on paper with a brush, the Greeks and Romans were unacquainted with paper making and used tablets covered with wax, on which they wrote with a pointed stylus.

Writing inks have long been known. Pliny, Vitruvius, and other classical authors mention them, and Dioscorides gives a special recipe for making ink. It is a striking

coincidence that the ink of the Greeks and Romans was practically the same as that of the Chinese, and consisted mainly of fine soot worked up in a vehicle. The printers' ink of to-day owes its colour to the same pigment.

The (German) word for ink (*Tinte*) comes through *tinge*, from the Latin *tingere*, to dye or to colour. Thus an ink means a liquid that will produce a colour.

Old deeds and other parchments show us that even in the early Middle Ages the art of ink making had been brought to a high degree of perfection. Letters 800 years old, indeed, are less faded in many cases than those of a much more recent date. When we see a MS. which has become almost illegible in fifty years or less, we are inclined to think that the knowledge of ink manufacture has gone backwards instead of forwards. We must not forget, however, that the durability of an ink depends not merely on itself, but also on the substance it is written on. Many of the substances now used in preparing papers, such as lime and chlorine, have, even when present in very small quantities only, a destructive effect upon an ink which if used on pure parchment would last as long as the monastic productions of the Middle Ages have done. All our bleached papers contain chlorine, which sooner or later destroys the paper. It is thus useless to write documents intended for long preservation with indelible ink if paper is used to write them on. Our modern books, printed without exception upon paper that has been bleached with chlorine, will disappear in a few centuries by the disintegration of the paper. This defect attaches particularly to a sort of paper much used now on account of its cheapness, that made from wood pulp. This in a few years turns brown, and becomes so brittle that it breaks when folded. Printing ink, on the other hand, which depends for its colour on carbon, is practically imperishable.

People are now becoming alive to the disadvantages of such paper, and are printing important books on paper which is free from every trace of free chlorine. The durability of unbleached vegetable fibre is well exemplified by the linen wrappings of the Egyptian mummies. Woven four thousand years ago, it is now scarcely brown, and is still fairly strong. If the ancient Egyptians had written on such stuff with good ink the writing would be plain to this day.

The manufacture of ink has been carried on empirically until very lately. The first to apply scientific knowledge to the manufacture was Lewis, at the end of the eighteenth century. Since his time Berzelius and Bottcher have done a large amount of work at the subject.

Changes in the methods of manufacture of ink have been accompanied by two other movements which have had great influence on it. One of these is the substitution of smooth machine-made paper for the grey or brown hand-made paper. This glazed paper requires for its manufacture a very powerful bleaching of the raw material, with the result that it invariably contains chlorine or lime. It has thus become important to find inks that will resist the slow action of these substances. This may appear a very simple matter, but is in reality a difficult one. The second movement was the substitution of the steel pen for the quill. While in former times the goose-quill only was used for writing and the raven-quill for drawing, the steel nib is now almost universally employed for both. The substance of a quill is extremely resistant to chemical action. Steel, on the other hand, is readily corroded by very many things. Even very dilute acid in the ink will soon make a nib unusable. Before inks were invented which would not act on iron, many attempts were made to devise a protective coating for the

nib, by covering it with copper, silver, or even gold. This coating, however, soon gets worn off the tip of the nib, even in using the smoothest paper.

We have called the manufacture of ink an art. Many may smile at the designation, but we shall adhere to our nomenclature. It is not easy to make an ink fulfilling every requirement that may be demanded of it, especially as we are even now to a large extent in the dark as to the exact chemistry of ink manufacture, although distinguished chemists have not thought it unworthy of them to work at the subject.

## II.

## VARIETIES OF INK.

By ink in general we understand a coloured liquid intended to make durable signs on any surface.

Inks may be classified according to their uses into several fairly distinctly defined groups, as follows:—

*Writing Inks*, for use with a pen, closely allied to which are the *Copying Inks*, also for use with a pen, but from which impressions can be reproduced. One of the latest species of copying ink is *Hektograph Ink*, which allows many copies to be made from an original written upon a specially prepared ground.

*Ink Powders* are powders which produce ink by mere solution in water.

*Ink Pencils* are closely allied to these. On slightly damp paper they make marks resembling those made with aniline inks.

*Drawing Inks* produce drawings by means of an ordinary pen or a drawing pen.

*Lithographic Inks* are used solely for writing and drawing

on lithographic stone, and these must resist the corrosive fluids used by lithographers.

*Marking Inks* are used as a substitute for the old practice of embroidering names or initials on the garments.

*Printing Colours* include those used for marking guiding lines for embroidery, as well as those for india-rubber stamps, although the latter differ somewhat from most of the others. To printing colours, in the wider sense of the word, belong also the compositions used for typewriter and tape-machine ribbons. Many of them permit of copies being taken, so that they are closely connected with the copying inks.

Among ink specialities we include gold and silver, and sympathetic inks, and every ink maker ought to know how to make these varieties, although they are not much in demand.

We can easily see that the number of inks and allied products is considerable. If we were to reproduce all the recipes that have come before us we should fill several volumes of the size of the present one.

Our knowledge of ink making is almost purely empirical, as we are at present to a very large extent ignorant of the exact chemistry of the subject. Most inks are combinations of metals with organic matter, especially with tannins. It was formerly believed that only one of the substances contained in a tanning material was able to produce the black substance the presence of which is essential to the constitution of the ink, but we have now become aware that there is a vast number of such substances with most of which we are only very imperfectly acquainted. This explains the multiplicity of the recipes, and is the only possible reason for the remarkable fact that recipes vary enormously in the proportions given, although the substances they name are exactly the same. One

recipe assigns a prominent place to an ingredient which the other relegates to a very minor share in the composition of the ink. In ink manufacture we have not got beyond the recipe-making stage, and every maker will do well to experiment with the new recipes he may come across, and try to improve them. There can be no doubt that there is a vast field for original research in ink making, and it would be highly remunerative. Few articles of daily use are sold at so high a profit as ink. Even a small sale will keep a man comfortably. In view of the failures that we all experience sometimes in our ink making, it is quite certain that every step forward which we can make, be it ever so small, will be of material value to its discoverer and to the trade in general.

## III.

## WRITING INKS.

In considering these inks first, we must begin by setting forth clearly what properties are required in ordinary writing fluid. They are four in number, and will now be considered *seriatim*.

1. *Depth of Colour.*—The writing must at once or very quickly show a strong and decided hue of the colour which the ink is intended to produce.

2. *Freedom of Flow.*—The ink must flow readily from the pen, so that the finest lines and characters may be executed. The ink must not be thick, or form hard crusts when it dries upon the nib. This occurs sometimes with perfectly good ink, and is then merely a sign that the ink has become too concentrated by evaporation and requires dilution with water. If, however, the addition of water does not make matters right the ink is bad, whether

it was so originally or not. This freedom of flow cannot of course be so perfect with a copying as with an ordinary writing ink. Copying inks are thicker and slower to dry than ordinary writing inks. Many complaints reach dealers from careless customers who have used copying ink when they had no intention of taking copies, and have found the two sides of a letter, for example, stick together so firmly that they were illegible when separated. Copying ink must always be diluted if it is to be used as a substitute for ordinary ink. It will not lose its special properties entirely even then.

3. *Durability*.—A good ink should keep its colour unchanged for a long time, even if the paper gets damp or wet. This is a quality which comparatively few inks possess. A good ink must gradually dry in the air to a brittle mass, and must not go mouldy, even after great dilution. This last condition is easily fulfilled. The main constituents of many inks are powerful antiseptics, and in any case antiseptics can always be added to them.

4. *Indelibility*.—For certain purposes, such as for documents that will possess a historical interest, it is necessary that the ink should be able to resist not merely the ravages of time, but also deliberate attempts to efface it. To secure absolute indelibility is impossible, for resistance to every agent that could possibly be employed is a property that no substance we know of, or are at all likely to become acquainted with, possesses. While no ordinary writing ink, however, offers any considerable resistance to chemicals, certain inks, especially those which owe their colour to carbon, are capable of withstanding them extremely well. Printers' ink, indeed, can only be destroyed by destroying the surface printed on as well. Printers' ink, however, can hardly be produced in such a condition as to be usable with a pen. Some dark-coloured substances of organic

origin, also the so-called humus-bodies, play a very good second to carbon in respect of indestructibility.

The first three of these four qualities may be reasonably demanded of any ink professing to be a good one, and it is the business of our trade to make inks possessing good colour, freedom of flow and a reasonable degree of durability, and no others.

We can classify writing inks either according to colour or to composition. The names red ink, blue-black ink, etc., are examples of the former method, and such appellations as chrome ink, hematoxyline ink, and others, illustrate the second. Several of these names, however, are misleading. Many inks are sold as alizarine inks, for example, when neither madder nor alizarine has been used in their manufacture. We have no intention in this work of binding ourselves to any particular classification too strictly, as we see no particular advantage to be gained by so doing. We shall describe the inks under their colours in an order depending partly on the method of manufacture and partly on similarity between the recipes. As black is the most important of all the writing inks we shall devote more space and attention to it than to the rest.

## Black Writing Inks.

Black inks differ greatly in chemical composition, and can be divided into two sharply marked-out groups—those containing tannin, and those not. The first class can be further divided, according to the raw material used, so that we have catechutannic acid inks, gall nut-tannic acid inks, etc. The inks free from tannin, or those which contain it with other substances, can also be divided on the same plan into chrome inks, logwood inks, and so forth. The differentiation of the two main classes is not, however,

absolute, as inks made from dye-woods, which we have put in the second class, often contain tannin. The black writing inks which have been longest known and which are the most important are the tannin inks, and they are the cheapest to manufacture. In spite of this no maker should confine himself to such inks, as they have not, as a rule, the degree of durability that is now required of an ink. In fact they can already be regarded as antiquated, and as destined to be soon disused altogether.

## Tannin Inks.

In nearly every case these inks contain tannate of iron. Tannin being a very abundant substance in the vegetable kingdom, it follows that a very large number of plants can be utilised for ink making. It must be borne in mind, however, that although the various tannic acids of different plants are closely allied, they, and therefore the inks made from them, show well-marked differences in properties. Some of them give bluish compounds with iron, and some a characteristic greenish colour which only very slowly changes to the deep black which we are accustomed to in a good ink. Tannin inks which write a black at once usually cannot penetrate the paper, and have consequently no durability whatever.

The following may serve as a list of the chief raw vegetable materials used for making tannin inks: gall-nuts, valonia galls; barks of oak, sumach, poplar, willow, fir, and horse-chestnut; the wood of the elm and horse-chestnut, as well as sloes and buckthorn berries. This list makes no pretence of being complete, but only gives the more important materials. It is possible to use any plant or part of a plant for making these inks provided it contains tannin.

Before describing more minutely the properties of these tannin-containing bodies, we propose to make the reader acquainted with the chief chemical properties of the tannins themselves, as a necessary preliminary to the comprehension of the formation of the inks, and as a means of enabling him to make experiments and improvements for himself.

We proceed then to speak of the tannins or tannic acids as they occur in the form of definite chemical compounds.

## Tannins.

All the higher plants contain acids. All these acids are soluble in water, and many of them are characterised by a rough and astringent taste, and are called tannic acids. If the solution of one of them is mixed with one of gelatine a precipitate is formed, which consists of tannate of gelatine. Tannin behaves in a singular manner with egg albumen and also with fresh animal skins. If the hide of an animal is dipped into a solution of tannin it will gradually absorb the tannin, and acquire the property of keeping for long periods without putrefying, even when in contact with water. The hide is also made pliable and smooth, and is called leather.

Another property which all the tannic acids have in common is to form bluish-black or greenish substances when brought into contact with iron salts. These coloured bodies are very prone to decompose and become mouldy, so that a badly made tannin ink soon becomes utterly worthless.

## Quercotannic Acid.

This is the commonest of all the tannins, and occurs in every part of the oak, but particularly in those morbid products of the tree known as gall-nuts. We also have

quercotannic acid in Chinese galls, in sumach (*Rhus coriaria*), in sloes, and in the wood and bark of the pine.

Quercotannic acid is freely soluble in water, spirit, or ether, or in mixtures of them. In preparing it in a state of purity, however, it is best to use only ether as a solvent. Quercotannic acid is best prepared from gall-nuts as follows: The galls are coarsely powdered and put into a separating funnel stuck in the neck of a bottle as shown in

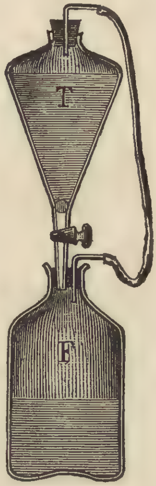


FIG. 1.

Fig. 1, where T is the funnel and F the bottle. The tube shown permits air to pass from F to T, as liquid passes the other way. A filtering plug of cotton wool having been put into the neck of T, the gall powder is put into it and covered with ether. Care must be taken not to use ether near a naked flame as it gives off a highly inflammable vapour. The corks and tube are then fitted as shown, to prevent loss of ether by evaporation. When the ether

has all drained into the bottle rinse the galls with as much water as will increase the bulk of liquid in F by one-half. There will now be two layers of liquid in F. The lower is brown and contains the tannin, while the upper layer is nearly pure ether and can be used again. This ether having been decanted, the tannin solution is poured into a shallow basin and left, with a sheet of paper as a lid to keep out dust, until the ether has dried up, and only a pale yellow powder remains, which is pure tannin plus a little water. The tannin is then dried under a bell-jar, which also contains a dish of concentrated sulphuric acid. The tannin finally becomes a nearly white amorphous powder, having an extremely astringent taste. Tannin does not crystallise, so that the expression "crystallised tannin," sometimes seen in price lists, is misleading.

If an aqueous solution of tannin is exposed to the air, it soon becomes covered with a thick crust of mould, and in time the tannin is all converted into gallic acid. Quercotannic acid, if heated dry, is partly carbonised and partly changed into pyrogallic acid which volatilises.

## Gallic Acid.

This acid occurs in divi-divi, in mango kernels, and, to a small extent, in gall-nuts. If a decoction of divi-divi in boiling water is allowed to cool, it deposits brown crystals, which, by solution in water, filtration through animal charcoal and recrystallisation, become white. It is, however, much better to make gallic acid from gall-nuts by crushing them and leaving them in a damp state until the mould, which rapidly accumulates upon them, has converted the quercotannic acid into gallic acid. This can then be dissolved out with water and purified by crystallisation.

Gallic acid is sharply differentiated from quercotannic acid by precipitating neither gelatine nor albumen. With ferrous salts it forms a deep blue solution, and on this property is based the value of gallic acid to the ink manufacturer.

### Pyrogallic Acid.

When gallic acid is kept at between 210 and 215 deg. C. it is gradually converted into pyrogallic acid. Distinctive properties of this are the precipitation of the metal from solutions of gold or silver and the formation of a bluish-black colour with protosalts of iron.

### Catechutannic Acid.

*Mimosa catechu*, a tree indigenous to India, provides an extract known to commerce as cutch. The special tannin of cutch is prepared by boiling it in water and adding sulphuric acid to the decoction. A precipitate is formed, which is a compound of catechutannic with sulphuric acid. This precipitate is mixed with carbonate of lead and boiled in water. The sulphuric acid remains undissolved as lead sulphate, and the catechutannic acid can be crystallised from the filtrate. A simpler method is to extract the cutch with ether. Catechutannic is much like quercotannic acid, but is distinguished from it by giving a dirty green precipitate with solutions of iron salts.

### Kinotannic Acid.

This occurs in gum kino, and is a brown substance very similar to catechutannic acid, and forms a blackish-green compound with ferric salts. Fermentation converts it into kino red.

### Morotannic Acid.

This is deposited from a cooling decoction of fustic, the wood of *Morus tinctoria*. It has a sweetish astringent taste, and with ferrous salts gives a blackish-green precipitate. Heated it gives pyromoric acid, which has to it the same relationship that pyrogallic has to gallic acid. Moric acid is another acid present in fustic, and is probably related to morotannic acid in the same way that gallic acid is to quercotannic acid, and formed, like it, by fermentation.

The tannic acids we have just been describing are chiefly important to us from their action on solutions of salts of iron. Although this action is different with ferric and with ferrous salts, the difference is of little importance to the ink maker, for as all ferrous salts oxidise to ferric salts on exposure to the air, the final colour of the ink is always due to ferric iron. The following table shows the colours given by the various tannic acids:—

| Acid. | Colour with Ferrous Salts. | Colour with Ferric Salts. |
|---|---|---|
| Quercotannic | — | Blackish-blue |
| Gallic | — | Dark-blue |
| Pyrogallic | Blackish-blue | — |
| Catechutannic | Dirty green | Dirty green |
| Kinotannic | — | Blackish-green |
| Morotannic | — | Dark-green |

To get a deep black ink we must always use a gall-nut tannin.

Inasmuch as the chemically pure tannic acids are too dear to be used, in practice we shall never get any of the above-named colours in full purity, but always with a tendency to brown or black, owing to the action of the

other substances present. This is, however, immaterial, as all that we require is that the colour should be very dark and also durable.

The tannin-containing bodies which we use come upon the market in many different qualities, so that we must describe the most important of them fully enough to prevent our readers from being cheated in purchasing. As iron salts are essential for making tannin inks, we shall describe those salts which we use, so that our readers may make them for themselves if occasion should arise.

## IV.

## RAW MATERIALS OF TANNIN INKS.

### Gall-nuts.

Gall-nuts are morbid growths on the leaves of various kinds of oak caused by the sting of the gall wasp. The gall-nut is formed round the egg of the wasp which is laid by the sting, and the metamorphoses of the larva generally take place inside the gall, which is only deserted by the insect when it has reached its fully developed state; then it bites for itself a hole of escape. In trade, the chief distinction made with galls is into pale and dark, but they are classified also as white, yellow, green, blue and black galls. The best galls are those from which the insect has not escaped, *i.e.*, which are unperforated, as those galls contain the highest percentage of tannin. Good black galls contain up to 27 per cent. of tannin, included in from 35 to 37 per cent. of soluble extractive. The form of the galls is nearly spherical, and their size varies from that of a pea to that of a small walnut. A good gall must be heavy and show a compact mass when cut through. If the gall is very light and filled with a crumbly mass it is

of poor quality, as its content of tannin will be low. Experience has shown, too, that galls from southern countries are richer in tannin than those from the north.

The best galls are the Levantine galls, also called Aleppo galls. Next to them in quality are Morea, Smyrna, Marmora and Istrian galls. In the third rank are the French, Hungarian, Italian, Senegal and Barbary galls.

The signs looked for in the trade as denoting a good gall are almost perfect sphericity, a size not exceeding that of a cherry, a rough, unperforated exterior and considerable weight.

Chinese galls have a smooth surface, often showing a reddish hue, and readily peeling off. Inside is a brown substance full of the dead larvæ of insects. It is not yet known with certainty from what plant these galls come or what insect produces them.

### Knoppern.

Ordinary galls are produced on the leaves and young stems of the oak, but there is a kind produced by the gall wasp stinging the immature cups of the acorns. The result is the development of a gall instead of an acorn.

Knoppern are misshapen brown masses. They are harvested mostly in August, and the chief place of production is Hungary. The Bakony forest, situated between the Lakes of Neusiedler and Platten, yields an enormous quantity of knoppern. Large amounts come also from the oak forests of Asia Minor.

Knoppern come on the market both whole and crushed. Chemically they are practically the same as the other galls, and, like them, contain a high percentage of tannin which secures them great employment in the leather, dye and ink trades.

## Tanners' Barks.

The crushed bark of the elm, oak, pine, poplar, willow, etc., is largely used in tanning. The bark, after having been once used, is spread out by the tanners and dried for use again. The dried bark ferments, and its quercotannic acid becomes gallic acid. Tanners are agreed that quercotannic acid makes much better leather than gallic, which has a tendency to produce brittleness. For ink making, however, they are of equal value, so that the once-used bark should be bought from the tanners by the ink maker.

## Gall Extract.

Gall extract, otherwise called tannin extract, is on the market in the form of shining blackish-brown masses, having a very astringent taste. It is made by boiling in water galls, knoppern, fresh bark, and other tanniniferous vegetable substances, and carefully evaporating the decoction to a syrup, which, on cooling, sets to a brittle mass. Tannin extract is now made on a large scale by boiling down the decoction in vacuum pans.

A good extract should consist of little besides tannin, and must dissolve completely in water without any carbonaceous residue, giving a very astringent solution. When it is not too dear it is a splendid material for ink making, and to be recommended especially to ink manufacturers who have no space for storing large quantities of galls. Besides, the use of the extract simplifies the ink making considerably.

It must be remembered that the extract is very prone to mould in damp air. It should be kept in a dry room in casks or boxes lined with strong paper and with well-fitting lids.

## Cutch and Gambier.

This is also known as Japanese earth (*succus catechu* or *terra japonica*). It is obtained in the East Indies from the fruits and twigs of *Mimosa catechu* by boiling down a decoction of them. The chief cutch markets are Bombay and Calcutta, and it is divided into yellow and brown cutch.

Yellow cutch (gambier) is sold in dice-shaped pieces, which yield their colour to boiling water and give it a sweetish astringent flavour. It is better for dyers and ink makers than the brown kind.

Brown cutch is closer and heavier than the yellow variety, and the dark brown, shiny, sticky lumps yield a reddish-brown decoction.

Cutch contains catechutannic acid and variable quantities of japonic acid. There is more of this latter acid in brown than in yellow cutch. This is the reason why yellow cutch is better for our purposes, as japonic acid is of no use for ink making. The following is the percentage analysis of the two sorts:—

| | Yellow. | Brown. |
|---|---|---|
| Tannin | 54.5 | 48.5 |
| Extractives | 34.0 | 36.5 |
| Mucilage | 6.5 | 8.0 |
| Insoluble matter | 5.0 | 7.0 |

A purified cutch may be had but rarely. It is entirely soluble in water, and is to be preferred even to yellow cutch. The great demand for it caused the production of an adulterated extract in France. This rubbish is called *cachou épuré*, and consists of brown catechu mixed with 40 per cent. or more of its weight of ox blood.

## Gum Kino.

This is a brownish-red, brittle solid which gives a beautiful reddish-brown solution with water or alcohol. The chief ingredient is kinotannic acid. The following are the principal sorts found in commerce, with the name of the plant from which each is obtained:—

| | |
|---|---|
| African kino . . . . | *Drepanocarpus senegalensis.* |
| East Indian kino . . . | *Nauclea Gamber.* |
| Columbia kino . . . . | Unknown. |
| Australian kino . . . . | *Eucalyptus resinifera.* |
| Jamaica kino . . . . | *Cocoluba nucifera.* |

The first of these is the best gum, but it is very rarely to be met with unadulterated. To denote its purity more precisely it is also called Gambia gum.

## Fustic.

This is the wood of *Morus tinctoria*, and is indigenous to the West Indies. It contains morotannic acid. The sumachs, *Rhus coriaria* and *R. cotinus*, probably contain the same or very similar colouring matters as fustic. The fustics are used for yellow dyeing and also (with iron salts) for dyeing black. They give dark blackish-green inks.

We thus see that the whole manufacture of tannin inks turns on the colours which the various tannins give with iron. Hitherto the expense of purification has prevented the use of pure tannins in ink making, and has hence made it impossible to determine exactly the proper proportions of iron salt and tannin.

## Iron Salts.

The commonest of these is green vitriol, ferrous sulphate. The ferrous salts have for a base ferrous oxide,

while that of the ferric salts, the sesqui-oxide, contains a larger percentage of oxygen. Ferrous salts have a sea-green colour, and pass into ferric salts by absorbing oxygen from the air. Ferric salts are brownish-red. Green bottle-glass contains ferrous, brown bottle-glass ferric, oxide.

### Green Vitriol.

This is offered for sale in the form of large and beautiful sea-green crystals, which have an unpleasant, metallic, astringent taste, dissolve easily in water and, by long exposure, crumble to a rust-coloured powder of basic sulphate. Green vitriol is now so cheap, being a bye-product of several chemical manufactures, that it does not pay the ink maker to prepare it for himself. We may, however, describe how the salt can be prepared free from ferric iron if necessary. Pour dilute sulphuric acid on old nails, hoop-iron or other scrap, and as soon as the evolution of gas has ceased, filter the solution while it is still warm (it becomes hot of its own accord), and mix the filtrate with its own volume of strong spirit. The spirit throws down a pale green powder, which is pure ferrous sulphate. The precipitate is filtered off, dried in filter paper, and kept in a closely stoppered bottle.

Inks made with ferrous sulphate in time contain ferric as well as ferrous tannate. Those made according to antiquated recipes, by mixing solution of iron in strong vinegar with decoction of galls, are also ferrous inks.

### Ferric Sulphate.

This is prepared by mixing a solution of green vitriol with some nitric acid, and boiling. Unless too much nitric acid has been used we get a rusty-looking precipitate, because ferric oxide requires more sulphuric acid to dis-

solve it than ferrous oxide. This precipitate is basic ferric sulphate. We can either filter off, or carefully add sulphuric acid and warm it until it redissolves. The addition of any excess of nitric acid is carefully to be avoided, as free nitric acid will gradually bleach ink made with solutions containing it.

These pure salts are only worth preparing for use in original experiments, as they cost too much to be used in preparing ink for sale. Such experiments should, however, be made by every ink manufacturer who wishes to improve his business, especially if he wishes to work with tanniferous material with which he is not familiar. Ferric sulphate should be free from excess of sulphuric as well as of nitric acid, as acid fluids behave to tannins very differently from liquids not containing an excess of acid.

## V.

## THE CHEMICAL CONSTITUTION OF THE TANNIN INKS.

The tannic acids are always used in the form of the vegetable raw material. Hence the iron combines not only with tannic acid, but with other substances present in the vegetable matter, whereby the colour and other properties of the ink are modified.

According to the extensive researches of Bostock, which, however, were carried out a considerable time ago, the following reactions take place when a decoction of galls is mixed with a freshly prepared solution of ferrous sulphate.

The ferrous oxide combines with quercotannic acid, gallic acid, mucilage and with the extractives. The compounds with the acids are those which give the necessary colour, but the others deserve attention for several reasons.

It is these which often make an ink flow too thickly, and which impart the tendency to mould. Moreover, an ink which contains combinations of iron with mucilage or extractives also quickly loses its colour, and deposits a black sediment consisting of those compounds. Its precipitation leaves the ink almost colourless, as it entangles and carries down with it the coloured particles of tannate of iron, which, while suspended in the liquid, give the colour to the ink.

Many experiments show that the tannic acid is the only constituent of gall decoction which is of any value to the ink maker. If, for example, a cold infusion of galls is made and then kept boiling for a long time, a flocculent precipitate is formed, which consists of extractives coagulated by the boiling. If it is filtered off and the clear solution is exposed to the air, it becomes very mouldy in a few days. The fungi feed on the solution, and thereby produce in it important chemical changes. They convert the quercotannic into gallic acid, and destroy the soluble extractives almost entirely. In a few weeks indeed the liquid may be regarded as a fairly pure solution of gallic acid. If we then filter, and boil to kill the spores, we obtain a liquid which gives with solution of ferrous sulphate a fine blue-black ink, which will keep for months in an open vessel without showing the least sign of mould. The ink will, however, gradually turn pale and deposit a black sediment, because the fluid is not dense enough to keep the tannate of iron in suspension. These experiments show that the tannate and gallate of iron are present in ink, not in solution but in the solid state. The liquid must therefore be dense enough to keep the particles from settling, and, if necessary, bodies must be added which, while without action on the colour, augment the density. For this purpose we use either gum-arabic or dextrine, and also, although it is a less suitable

substance, sugar. Dextrine is much cheaper than gum-arabic, but has the great fault of being hygroscopic, so that the ink dries slowly on the paper. The use of sugar is unadvisable, not only on account of its price but because it favours the growth of mould, when the ink becomes a thick, stringy mass and can no longer be used.

In writing with inks made with ferrous sulphate we observe that the letters are at first bluish or greenish, but turn to a deep black in time. This change of colour results from the oxidation of the ferrous to ferric tannate, which has a darker colour than the ferrous compound. If the ink is made with ferric sulphate it writes black at once.

On account of the variable amounts of tannin contained in the raw materials, it is impossible to calculate the amount of iron salt required for any given weight of galls, oak bark, etc. Hence we find in recipes great differences in the relative quantities given. In our opinion nearly all recipes direct the use of much too large quantities of ferrous sulphate, and thus when the writing turns yellow or rusty the cause is to be found in the presence of an excess of iron salt which gradually decomposes the black tannate, so that at last nothing is left on the paper but basic ferric sulphate. This substance is also the cause of the yellow marks seen on linen which has been stained with ink and then repeatedly washed.

According to experiments which have been made on the properties of various inks in connection with the relative amount of galls and ferrous sulphate used in their preparation, it has been found that equal weights of galls and ferrous sulphate gave a very fine black ink, but that the characters soon turned brown and rusty. With still larger quantities of the vitriol the ink is still black, but very deficient in keeping power. The reason of this is that such an ink contains green vitriol in an unchanged state.

This oxidises on the paper, forming the brown basic sulphate. This brown can be easily got by simply writing with a solution of ferrous sulphate alone. The freshly dry letters are invisible, but exposure to the air soon converts them into the brown basic sulphate.

We shall find, on the other hand, that quantities of ferrous sulphate much less than the weight of the galls will still give a good deep black ink, for the extremely finely divided state of the tannate of iron gives it such great colouring power that a small quantity only of it is needed.

If we write on paper with only decoction of galls, the writing is at first hardly visible, but in time it will become brown, and easily legible. In one special case, however, to be presently described, the writing may disappear altogether. The tannins have the property of gradually turning brown, forming the humus-bodies which we see in the soil and in rotten wood. This change is greatly hastened by the presence of alkalies. Now paper always contains more or less lime, and this alkali helps the formation of the humus and the appearance of the writing. If the writing done with gall decoction is wiped over when dry with a sponge just damp with solution of washing soda, the brown letters will appear very quickly. But when the paper contains free chlorine, the writing will develop feebly or not at all. Such paper will destroy the colour of even the very best ink in time, as no organic dye can withstand chlorine, not even indigo itself. Such badly made paper also contains the seeds of its own destruction.

It is thus not difficult to decide whether an ink should contain an excess of iron salt or an excess of tannin. In the first case it will turn brown, and become nearly illegible. In the second it will remain black for a very much longer period. It must not be forgotten, however, that an excess

of organic matter makes the ink liable to mould, even after it has dried on the paper, so that the colour fades. Hence to such inks a disinfectant must be added.

The disinfectant ink makers make the most use of is carbolic acid, which is very cheap and is an unsurpassable preservative for all inks.*

Pure carbolic acid crystallises in long colourless needles, having a very penetrating odour, and easily soluble in water. The presence of as little as one-hundredth of a per cent. of carbolic acid will preserve even the most putrefiable liquid perfectly. As the acid evaporates slowly when exposed to the air, however, rather more than this proportion should be present in an ink, but never so much that its smell becomes perceptible. The acid may be made to contribute somewhat to the colour of the ink, as it forms a violet compound with ferric sulphate.

Many other disinfectants exist, such as salicylic acid, borax, etc., which are without smell, and so do very well for food, but are not suitable for ink. A quantity of carbolic acid that the most delicate nose cannot perceive is quite enough to preserve the ink.

It is probable that the huge amounts of sulphate of iron which we find in nearly all the older recipes are intended to act partially for preserving purposes, as the salt is a disinfectant itself. We have, however, pointed out the very grave objections to using excess of iron salt in a tannin ink. No one nowadays, when we have such a perfect preservative as carbolic acid, will think of making the iron salt do the work of an antiseptic as well as that of a colouring agent.

Although the tannin inks are the most liable to go bad of any, carbolic acid should not be added to them alone, but to all inks, for they are all putrefiable to some extent.

* See page 89.

The expense of so doing is very trifling, and the value of the addition can be appreciated by any one who will reflect that it absolutely guarantees that none of the ink which he manufactures will go bad either in his hands or in those of his customers. An exception to this rule, though, is found in the case of the aniline inks, which require no disinfectant, the dye itself being one.

As regards the amount of carbolic acid to be employed, one pound will preserve 1,000 gallons of ink. For the sake of perfect safety, however, more is used, say from 4 to 8 lb. per 1,000 gallons.

## VI.

## RECIPES FOR TANNIN INKS.

*N.B.*—THE QUANTITIES GIVEN IN RECIPES IN THIS BOOK ARE IN PARTS *BY WEIGHT* UNLESS THE CONTRARY IS DISTINCTLY STATED.

Few recipes consist simply of tannin material, iron salt, and thickening. Most of them mention other ingredients, although it is often impossible to see what influence these can have on the colour of the product.

We proceed to give a collection of first-rate recipes, beginning with ferrous inks, which have long been made of first-rate quality, and proceeding to other tannin inks subsequently.

### A.—PURE TANNIN-IRON INKS.

*Brande's Gall Ink.*

| | |
|---|---|
| Aleppo galls | 3 |
| Crystallised green vitriol | 2 |
| Gum-arabic | 2 |
| Water | 60 |

This ink is made cold. The crushed galls are placed in half the water, while the gum and the vitriol are dissolved separately in the other half. This solution is then poured into the vessel containing the galls. The resultant liquid can be used as ink at once, but it does not fully oxidise and acquire its deepest colour before the lapse of about two months. During this time it is occasionally stirred, and then, when the coarser particles have settled, the ink is bottled. The residue of the galls can be used again, and will make a good ink with—

| | |
|---|---|
| Green vitriol . . . . . . . . . | ½ |
| Gum . . . . . . . . . . | ½ |
| Water . . . . . . . . . . | 15 |

This method of manufacture is extremely simple, but one or two modifications greatly improve it. As the presence of the woody fibre of the galls is injurious they should be placed in a bag, which should then be hung in the water with two-thirds of its bulk immersed. The extraction of the tannin then goes on very fast, and all insoluble matter remains in the bag.

We have also in the ink many other extractives from the galls, and it is very liable to mould and to thicken. When the latter phenomenon occurs the whole ink is converted into an oily, spinning mass, which clings to the nib and cannot be remedied by filtration, but in most cases it can be cured by boiling it up with one-twentieth of its volume of strong gall decoction for two or three minutes.

We have by means of numerous trials so far improved Brande's ink that it responds fairly well to all requirements which can be made of a cheap product. The ink must be regarded as a cheap ink only, but it is an excellent writing fluid if a very dark colour is not essential.

*Improved Brande's Ink* (*Lehner*).

| | |
|---|---|
| Galls or knoppern | 1,200 |
| Ferrous sulphate | 800 |
| Gum-arabic | 800 |
| Water | 24,000 |
| Creosote | 3 |

Cover the galls with part of the water, and dissolve the gum, vitriol and creosote separately in the rest of the water. Pour the solution on to the galls, and cover up the vessel. Stir every day for about three weeks, when the ink will have reached its full blackness, and can be bottled off. This ink will keep for years.

*Ure's Tannin Ink.*

This is a very deep black and very durable.

| | |
|---|---|
| Galls | 18 |
| Ferrous sulphate | 8 |
| Gum | 7 |
| Water | 145 |

Add 130 of the water to the powdered galls in a pan, and boil with constant stirring, to prevent the ink from burning, for two hours, adding water little by little at intervals to replace that lost by evaporation. The decoction is then allowed to cool, and filtered through a linen bag, doubled or trebled if necessary, and sometimes with a filter paper inside. The bag is suspended by the frame shown in Fig. 2, the spikes going through the linen. While the filtration is proceeding we dissolve the vitriol and gum in the remaining 15 parts of water, and pour the solution into the filtrate.

The ink does not develop its full blackness at once. To

make it keep, a little carbolic acid should be added or some oil of cloves, or even a little gas-tar. Carbolic acid, however, is the best thing to use. Gas-tar was substituted when carbolic acid was expensive, but its use is now obsolete and to be avoided.

*English Counter Ink.*

| | |
|---|---|
| Galls | 20 |
| Ferrous sulphate | 5 |
| Gum | 5 |
| Water | 240 |

The water is divided into three parts—100, 80, and 60

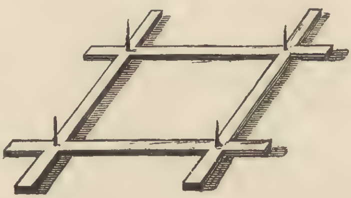

FIG. 2.

respectively. The galls are boiled in the largest portion for $1\frac{1}{2}$ hour. The decoction is poured off, and the second lot of water is boiled on the galls for an hour. It is then replaced by the smallest lot of water, which is boiled on it for half an hour. The first two decoctions are mixed, and the third is used to dissolve the vitriol and the gum. The whole is then mixed.

This practice of boiling the galls with several lots of water is highly to be recommended, as it ensures complete extraction. The ink is finally mixed with a little carbolic acid, and stirred once a day for a week. The ink becomes clear in a few more weeks and is then bottled.

To tell when an ink has cleared, *i.e.*, that nothing re-

mains suspended but the necessary colouring matter, mix some of it in a tumbler with water till it is transparent. No solid particles must then be visible to the naked eye, and on long standing a black sediment should form at the bottom of a pale yellowish-brown liquid.

*American Counter Ink.*

| | |
|---|---|
| Galls | 24 |
| Ferrous sulphate | 5 |
| Gum | 5 |
| Water | 200 |

The peculiarity of this ink consists in the fact that some of the vitriol is oxidised by roasting the whole of it before use. This is done over a fire in an iron, or better in an earthen, pan. The vitrol first loses its water of crystallisation and becomes white. It afterwards turns yellow from the formation of ferric sulphate. Over-heating converts some of this into the basic sulphate, which, being insoluble, is waste. We have therefore modified the roasting process somewhat with the best results. We mix two parts of water with one of concentrated sulphuric acid, and pour the mixture over twenty parts of ferrous sulphate. The whole is then slowly heated to the fusing point of lead. We thus obtain a substance perfectly soluble in water. Care must be taken that the heat expels all excess of sulphuric acid from the mass or the ink will corrode steel nibs, and be unusable.

*Karmarsch's Gall Ink.*

| | |
|---|---|
| Galls | 18 |
| Ferrous sulphate | 7 |
| Gum | 7 |
| Water | 64 |

The solids are powdered and left for a week in three-quarters of the water, with one daily stirring. The rest of the water is then added, and the ink is fit for use.

This ink is very good and cheap, but readily ferments, and should therefore be mixed with carbolic acid or with oil of cloves. The latter is an antiseptic and has a pleasant smell.

Gall inks attack nibs when not quite free from acid. Hence some recipes contain an alkali. An example of these is—

*Link's Steel-Pen Ink.*

| | |
|---|---|
| Galls | 224 |
| Ferrous sulphate | 96 |
| Gum | 80 |
| Water | 3,200 |
| Ammonia | 2 |
| Spirit | 128 |

The ammonia is to neutralise the free acid, and the object of the spirit is to prevent mould and to hide the smell of the ammonia. We think the spirit quite superfluous, as it not only adds to the prime cost of the ink, but makes the ink dry up. We have improved the ink as follows:—

*Link's Steel-Pen Ink (Improved by Lehner).*

| | |
|---|---|
| Galls | 112 |
| Ferrous sulphate | 48 |
| Copper sulphate | 2 |
| Gum | 40 |
| Water | 1,600 |

When the ink is made it is treated with carbonate of ammonia so long as a strong effervescence is caused. The reason for adding the copper sulphate is that this salt

covers a new nib dipped into the ink with a coating of copper, which protects it, as copper is much less easily corroded than steel. At least, we thereby guarantee the surface of the nib from rust, but the point very soon loses its copper coating through friction against the paper.

### B.—Gallic Acid Inks.

The gallic acid inks combine with a beautiful blue-black colour the valuable property of being far less liable to decomposition than those made from quercotannic acid. The speciality of the manufacture consists in the preliminary conversion of all that acid into gallic. This is done by simply allowing the galls or their decoction to ferment spontaneously. It is, however, often very inconvenient to have a big vat of decoction standing fermenting for weeks together. Hence we give the following very practical method of simplifying the work. A vat is nearly filled with the coarsely powdered galls or bark, and just enough water at from 20 to 25 deg. C. is then poured on to cover the mass. The contents of the vat mould with great rapidity, and the fungus fills the inside of the mass with a whitish felt and covers it with a green crust. The whole conversion into gallic acid is completed in from 8 to 10 days, when, to prevent further action, boiling water is poured over the mass to kill the ferment. The solution of gallic acid is then drawn off by means of a cock. It gives ink of a fine blue-black colour and of great durability.

The names under which these gallic acid inks come on the market are as various as the recipes for making them. We here give some of the best :—

*First Quality Gallic Acid Ink.*

| | |
|---|---|
| Gall-nuts | 50 |
| Ferrous sulphate | 10 |
| Gum | 10 |
| Water | 2,000 |
| Carbolic acid | 2 |

The crushed galls are soaked in the water and allowed to ferment. This often takes some time, especially in the winter. It is a good plan to inoculate the mass with the mould from a piece of mouldy bread or leather. The fermented liquid is filtered, and the other ingredients dissolved in it.

*Runge's Gallic Acid Ink.*

| | |
|---|---|
| Galls | 8 |
| Water | 64 |
| Ferrous sulphate | 4 |
| Gum | 2 |

The larger part of the water is poured boiling over the crushed galls, which are then allowed to ferment for two months. The liquid is then drawn off, and the residue is rinsed with the rest of the water. The two solutions are filtered together and the gum is dissolved in the filtrate. The vitriol is then added in the form of concentrated solution.

*Bolley's Inks.*

Bolley, formerly professor at Zurich, has published the following recipes, showing great diversity in proportions:—

1.

| | |
|---|---|
| Galls | 125 |
| Ferrous sulphate | 24 |
| Gum | 24 |
| Water | 1,000 |

This, according to our experience, gives a good ink, but contains galls in excess.

2.

| | |
|---|---|
| Galls | 66 |
| Ferrous sulphate | 22 |
| Gum | 19 |
| Water | 1,000 |

Here the proportion of vitriol to galls is correct.

3.

| | |
|---|---|
| Galls | 62 |
| Ferrous sulphate | 31 |
| Gum | 31 |
| Water | 1,000 |

In this there is an excess of iron salt, and ink made from the recipe turns yellow sooner than those made from the first two.

## Stark's Ink.

Boil 100 oz. of Aleppo galls with 8 gallons of water, and dissolve in the decoction from 33 to 50 oz. of gum. When cold add 66 oz. of ferrous sulphate, 66 oz. of indigo-carmine, and 1 oz. of carbolic acid. This is a beautiful ink, but the indigo-carmine makes it an expensive one.

### *Cheap Gallic Acid Inks.*

1.

| | |
|---|---|
| Galls | 100 |
| Logwood | 30 |
| Dextrine | 40 |
| Alum | 12 |
| Ferrous sulphate | 45 |
| Soft water | 1,000 |

2.

| | |
|---|---|
| Galls | 58 |
| Dextrine | 40 |
| Ferrous sulphate | 40 |
| Soft water | 300 |

3.

| | |
|---|---|
| Japan galls | 180 |
| Dextrine | 120 |
| Ferrous sulphate | 85 |
| Indigo-carmine | 90 |
| Water | 2,500 |

4. (*School Ink.*)

| | |
|---|---|
| Japanese galls | 30 |
| Water | 720 |
| Dextrine | 36 |
| Ferrous sulphate | 10 |
| Pyroligneous acid | 2 |
| Logwood extract | 28 |

## Extra Cheap Iron Inks.

Leather cuttings can be used with great advantage for the manufacture of glue and ink. The cuttings are covered with water containing $\frac{1}{2}$ per cent. of hydrochloric acid, and left for a week. The liquid is then run off, and as much as possible is squeezed out of the leather. The leather is then treated for another week with another lot of dilute acid. The solutions are filtered and mixed, and enough ferrous sulphate is added to make letters written with the ink turn a deep black in a few hours. The ink is then exposed to the air for several weeks, to darken it, and finally bottled. The leather residues are first soaked and then boiled in water, and will yield a very good if rather dark-coloured joiners' glue, for which it may be possible to find a market.

# VII.

# LOGWOOD TANNIN INKS.

## Logwood or Campeachy Wood.

Logwood is a medium-sized tree, indigenous to the West Indies and the greater part of tropical America, and known by the name of *Hæmatoxylon campechianum.* The wood is red or dark brown, from the presence of a special colouring matter called hæmatoxylin, which is extracted by boiling water.

The decoction is dark red, and gives an intense dark blue-black with iron salts. Hæmatoxylin has a great affinity for ammonia, and forms with it crystals which are green to reflected and red to transmitted light.

Logwood comes upon the market in fairly large pieces, sometimes with the white sapwood still adhering to it, but sometimes freed from it. It is very easy to extract the colouring matter from ground logwood, and this is therefore preferred by ink makers; but wrongly, as it is so extensively adulterated with foreign woods and water that it can only be safely bought by an expert.

## Logwood Extract.

This can be highly recommended for use by the ink manufacturer, as it is very convenient, and its relative price is very small when we consider that the trouble and expense of preparing it are avoided. It can be roughly estimated that the extract is equivalent to four times its weight of the wood.

Commercial logwood extract occurs in the form of irregular pieces or flat plates with a shining dark-brown surface,

and readily soluble in water, leaving, if the extract is good, very little residue, which consists of substances coagulated by the heat of the evaporation.

Although logwood decoction or a solution of the extract will make ink with an iron salt and without any third substance, yet logwood is preferably used as an addition to tannin inks which are not black enough without it.

The logwood may either be boiled or macerated with the galls, or the two decoctions may be made separately and then mixed. If logwood extract is used it is dissolved in the least possible quantity of hot water, and added to the solution of the other ingredients separately made.

The logwood tannin inks have a splendid blue-black colour and fair freedom of flow. They also have the great advantage that they attack the nibs less than pure tannin inks, as the logwood probably forms a varnish on the pen when it is laid aside, which excludes the air and prevents rust.

### Campeachy Ink.

| | |
|---|---|
| Galls | 9 |
| Ferrous sulphate | 9 |
| Logwood shavings | 9 |
| Gum | 9 |
| Water | 180 |
| Vinegar | 180 |

Dissolve the gum, the vitriol, and the galls in the vinegar, and make a decoction with the logwood and the water. Then mix. The water which evaporates during the making of the logwood decoction must be replaced.

### Campeachy Extract Ink.

| | |
|---|---|
| Galls | 36 |
| Ferrous sulphate | 36 |
| Logwood | 9 |
| Gum | 36 |
| Water | 300 |
| Vinegar | 60 |

Proceed as above, and filter the finished ink.

### Ribancourt's Campeachy Ink.

| | |
|---|---|
| Galls | 16 |
| Logwood raspings | 8 |
| Ferrous sulphate | 8 |
| Copper sulphate | 2 |
| Gum | 6 |
| Sugar | 2 |
| Water | 200 |

The logwood is boiled with the water till half the liquid is evaporated. The decoction is filtered hot, and the other ingredients are dissolved in it. As soon as ink is cleared, which takes about three days, it is run off from the sediment and bottled.

### Campeachy Gallic Acid Inks.

These much resemble the inks last described, and practically the only difference is that they contain gallic instead of quercotannic acid.

### First Quality CGAI.

| | |
|---|---|
| Galls | 20 |
| Campeachy wood | 30 |
| Ferrous sulphate | 20 |
| Gum | 30 |
| Water | 130 |

Crush the galls, and let them ferment with 80 of the water for a fortnight. Then draw off the liquid, and rinse the residue with enough water to make the liquid and washings up to 100. The remaining 50 of the 130 of water is boiled on the logwood raspings till the solution only weighs 30. It is then filtered hot, and the vitriol and gum are dissolved in it. It is then mixed with the gallic acid solution. In a few days there will be a considerable precipitate. The supernatant liquid is an excellent ink of a pure black colour.

## Hæmatoxylin Ink.

This differs from the last chiefly in name. The following is the recipe:—

| | |
|---|---|
| Galls | 40 |
| Logwood | 50 |
| Ferrous sulphate | 30 |
| Gum | 25 |
| Water | 200 |

Leave the powdered galls with part of the water for at least three months in a uniformly warm room.

We differ here from the recipe, for a fortnight is certainly ample for the complete conversion of the quercotannic into gallic acid. If a longer time is allowed other changes set in, and the gallic acid is itself altered and much of it converted into substances quite useless for ink making. This is quite irrespective of the waste of time and capital involved in substituting thirteen weeks for two. Even if there were a little quercotannic acid left, that would not matter in the least. The logwood is then boiled for some hours with the gallic acid solution, adding water so as to keep the volume constant. The vitrol and gum are then dissolved in a little of the liquid, which is then aaued to the main mass.

## VIII.

## FERRIC INKS.

As already stated, many inks only acquire a deep black colour a considerable time after the writing has been done. The change is due to the oxidation of the ferrous to ferric tannate. As a necessary consequence of this many attempts have been made to use ferric salts only in the manufacture, so as to get an ink which will write a deep black from the first. The chief method is to roast the ferrous sulphate, *i.e.*, to oxidise it by heating it in the air before it is used. Our experiments, however, have shown that inks containing ferric iron only are of very little value. We prepared the ferric sulphate by boiling a solution of the ferrous salt with nitric acid or by dissolving the sesquioxide in sulphuric acid.

On adding to the ferric salt a decoction of galls, fermented or unfermented, and with or without logwood, an ink was obtained which wrote at once with a faultless lustrous black, but in time the characters lost their lustre and became of a brownish hue. Worse than all, however, the ink adhered so loosely to the paper that with a little care the writing could be entirely erased with a damp sponge. It was only after some years that the ink withstood the sponge to some extent. Probably the ferrous compounds penetrate the paper more deeply than the ferric salts, so that when the persalts are formed on the paper they are formed below the surface, and are hence protected by the fibre from removal with water. The browning of the writing done with a ferric ink is probably due to separation of part of the sesquioxide; this in the free state shows the reddish-brown colour which is so familiar in rust.

### Japan Ink.

This long celebrated ink principally consists of ferric tannate. It is made by roasting green vitriol at a moderate heat and then treating it with logwood extract and decoction of galls. It is of a deep black at first, but has all the drawbacks above noted as belonging to ferric inks. Like all other ferric inks, too, it does not flow very freely, and the nib must be carefully cleaned after use or it will soon be so encrusted as to be unusable.

The best iron inks are thus those made from ferrous sulphate. The writing soon comes to have the necessary amount of ferric oxide in it to make the writing black by spontaneous oxidation on exposure to the air.

## IX.

## ALIZARINE INKS.

If the name shows anything these inks should contain alizarine. Alizarine is a red colouring matter occurring in madder (*Rubia tinctoria*), but it is now always prepared artificially. It is very largely used in dyeing, especially in Turkey-red dyeing. Nevertheless, most of the so-called alizarine inks contain neither alizarine nor any other constituent of madder. We do not exactly know how such inks came to be called alizarine inks, but seeing that real alizarine inks are most excellent ones, we have little doubt that the name was adopted for fraudulent reasons, and to deceive chemists as well as the general public.

The inks so far described owe their colour to the presence of suspended and very finely divided quercotannate or gallate of iron. The sole object of adding gum is to keep the coloured precipitate in suspension, and if it is omitted a

black precipitate will soon form in the ink. The formation of this sediment can, however, be completely prevented by adding to the ink an acid which will dissolve it. For this purpose acetic acid is specially suitable, and we have here the secret of what are called alizarine inks. They are simply iron inks in which any precipitation of tannate of iron is prevented by acidification with acetic acid, or occasionally with sulphuric. The solution has generally a rather pale greenish or brownish colour, and the writing is at first green, turning in a few hours to a fine black. The process of blackening is a double one; the acetic acid evaporates in part, leaving the solid matter it had in solution behind it. Another part of the acid is neutralised, partly by the lime in the paper, but chiefly by the ammonia of the atmosphere. There is always lime in paper, from the water used in its manufacture. If a wet writing with an alizarine ink is put under a bell-glass with a dish of ammonia, the writing becomes black almost instantly.

Of course an ink which contains so strong a free acid as acetic or sulphuric must corrode steel nibs rapidly, but that only happens the first time the nib is used. If the ink is then allowed to dry on the nib it forms a protective coating which prevents further action. Naturally all excess of free acid should be avoided in the manufacture, if only for the sake of economy. An ink which has been accidentally made too acid may be brought to the right point by the cautious addition of ammonia. If too much alkali is added the object of adding the acid is lost, for it all becomes neutralised and solid matter appears in the ink. More of the too acid ink can be mixed in in this case. The best plan of all is to divide the ink which is too acid into two parts. One is then made neutral with the ammonia, and mixed with the other.

The "alizarine" inks have become very favourite writing

inks, partly because they leave no sediment, even when they have stood for years in bottle, and partly because they flow very freely from the pen—a matter of great importance for quick writing. The great objection to them is their pale colour. In some cases the fresh writing is barely visible. This can be got rid of by adding just enough of a solution of a very powerful dye, which is, in its turn, concealed when the ink turns black. Before the discovery of the water-soluble aniline dyes, indigo-carmine was the only substance available for this purpose. Until the artificial dyes were invented indigo- and cochineal-carmines had the greatest colouring power known, and both were therefore much used by the ink maker in spite of their high price. In fact no other dye is so suitable for his purpose as indigo-carmine, but we have now artificial dyes which will serve our purposes even in smaller quantities than will suffice of indigo-carmine, and they have therefore replaced it to a large extent. It is nevertheless suitable for every kind of ink, and in addition forms in itself an excellent ink both for writing and for stamping. We must hence describe it carefully.

## Indigo-Carmine.

Indigo is the splendid blue dye obtained by a fermentative process from *Anil indigofera*, a plant indigenous to India. Very many kinds of indigo come upon the market, and Bengal indigo is considered the best.

Indigo has a deep dark-blue colour and a characteristic coppery lustre. The following infallible tests of good quality should be carefully noted:—

The pieces must be light, and of a uniform colour, and show a uniform fracture. Sand and pebbles must be absent, and on rubbing with the finger-nail the coppery

lustre must appear distinctly. The pieces must not feel damp. They are often sprinkled with water to add to the weight.

To prepare indigo-carmine we must dissolve the indigo in sulphuric acid. This can only be done in the fuming or Nordhausen acid, and only when the indigo is quite dry. Having powdered our indigo fine (it is a mistake to buy indigo ready ground, as it is then usually adulterated), we dry it with the greatest care at a temperature which must not exceed 120 deg. C. at the highest. The acid is then poured on to the indigo while it is still warm. The quantity needed depends upon the purity of the indigo and on the strength of the acid. It is usually about four times the weight of the dry indigo.

The acid must be added slowly with constant stirring with a glass rod, and the indigo must be in a roomy earthen basin, because the act of solution is accompanied by much frothing. When all the acid is in, the basin is left covered up for twenty-four hours. By that time the conversion of the indigotin into sulphindigotic acid is complete, and the latter compound must be at once converted into indigo-carmine of inferior quality, as it would be mixed with substances previously mixed with the indigotin which have been carbonised by the sulphuric acid. To get pure indigo-carmine we dilute the liquid with 10 or 12 times its volume of pure water, and allow it to stand for a few days, till all the insoluble matter has settled to the bottom. The clear solution then looks black in large masses, but slender columns of it are transparent and of a splendid blue colour. It is decanted and evaporated without boiling, and at the same time neutralised with carbonate of potash. As soon as the effervescence due to the escape of carbonic acid has ceased we have a solution of pure indigo-carmine, which is potassic sulphindigotate. This salt can be got in the solid

state by very cautious further evaporation, but it is more usual to precipitate it with carbonate of soda, on the addition of which the indigo-carmine, being less soluble in saline solutions than in water, is thrown down. It is filtered off and dried, when it shows an efflorescence of the excess of soda.

Indigo-carmine when dry has a deep blue colour with a strong coppery lustre. It is extremely soluble, and a very small quantity of it gives an intense blue colour to the water. It is very difficultly soluble in alcohol or in saline solutions.

For ink making it is quite unnecessary to evaporate down the solution of indigo-carmine. As soon as the neutralisation with carbonate of potash is finished, the solution should be concentrated and preserved in bottles. It is, however, required in a solid state for water-colour painting and as a laundry blue or for india-rubber stamps. The above-mentioned efflorescence spoils the look of the solid substance, and can be prevented by adding glycerine to the mass. The hygroscopic qualities of the glycerine prevent the soda from crystallising, and make the dark blue of the indigo-carmine appear to the fullest advantage.

### Counter Alizarine Ink.

| | |
|---|---|
| Galls | 20 |
| Ferrous sulphate | 12 |
| Gum | 2 |
| Acetic acid | 200 |
| Indigo-carmine solution | 40 |

This green, readily flowing ink is made by soaking the powdered galls in the acetic acid, drawing off the solution after a few days, and dissolving the vitriol and the gum in a part of it, which is then added to the rest. Finally the indigo-carmine is added. It is best not to weigh it,

but to add it gradually till the ink writes a fine bluish-green at once. The ink is bottled as soon as this point is reached, and forms a clear dark-green solution.

Many ink makers use sour beer instead of vinegar, and thus get an ink which soon moulds on exposure. To avoid this, and at the same time save expense, crude pyroligneous acid should always be employed. The carbolic acid in this prevents any mould from growing.

### First Quality Alizarine Ink.

| | |
|---|---|
| Galls | 40 |
| Iron solution | 15 |
| Indigo-carmine | 5 |
| Gum | 10 |
| Pyroligneous acid | 10 |
| Water | 100 |

This, which is the best of all alizarine inks, and has no action on steel, is prepared from the above hitherto unpublished recipe, as follows:—

The galls are powdered and soaked in the water and half the acid for a week. The quercotannic acid is thus completely extracted, but none of it converted into gallic, as the pyroligneous acid prevents any fermentation. The iron solution is prepared from pyroligneous acid and scrap iron, left together for a week. This solution must contain enough acid to keep the acetate of iron in solution. To test this point a sample of the gall infusion is mixed with one-tenth of its volume of the iron solution. The thin column of the mixture should be clear and of a dark-green colour, but if the column is black and opaque more acetic acid is necessary, and the additional amount required must be ascertained exactly by adding measured quantities of pyroligneous acid, with constant stirring, till the liquid assumes the appearance described. From this the extra

amount wanted for the whole lot of ink can be calculated. Any necessary extra acid is then added to the gall infusion, the gum is dissolved in it, and the iron solution is then put in. Enough indigo-carmine is then added to give the required shade.

### Alizarine Indigo Ink.

The following is Prollins and Bley's recipe:—

| | |
|---|---|
| Galls | 20 |
| Indigo | 2 |
| Fuming sulphuric acid | 8 |
| Iron filings | 4 |
| Chalk | 4 |
| Water | 160 |

Boil the crushed galls with the water till the infusion weighs 40. Dissolve the indigo in the acid, add 40 of water to the solution, and then put it into the gall infusion. Then put in the iron filings, where they dissolve with evolution of hydrogen, the ferrous sulphate reacting with the quercotannic acid. The excess of sulphuric acid is then precipitated as sulphate of lime by means of chalk. A still better plan is to dissolve the iron in the indigo solution first, neutralising them with chalk, and adding the gall infusion after decantation from the sulphate of lime. The reason is that in the method first mentioned the calcium sulphate carries down with it some of the colouring matter of the ink. This method is simpler but more expensive than using sulphate of iron ready made.

### American Alizarine Ink.

| | |
|---|---|
| Powdered galls | 40 |
| Ferrous acetate | 15 |
| Gum | 10 |
| Pyroligneous acid | 10 |
| Indigo-carmine | 5 |
| Water | 100 |

We could give many more recipes for these inks, but they simply vary from those given and about to be given in the proportions of the ingredients, without giving any better inks.

### Real Patent Alizarine Ink.

| | |
|---|---|
| Aleppo galls | 84 |
| Dutch madder | 6 |
| Indigo-carmine | 2 |
| Ferrous sulphate | 10 |
| Pyrolignite of iron | 4 |

The galls and madder are boiled with water down to 240 of solution, and the other ingredients are added after filtering. The addition of the madder makes very little difference to the beauty or the durability of the ink, and it is now very difficult to get madder.

### Hager's Alizarine Ink.

In a roomy earthen dish (to allow for frothing) put 12 of fuming sulphuric acid, and add to it, little by little, 2 of indigo. Twenty-four hours after the indigo is all in, dilute with 16 of water, and dissolve in the solution 6 of clean iron filings. In the meantime boil 24 of Chinese galls with 300 to 400 of water, and dissolve 6 of gum and 3 of sugar in the decoction. Then add the other solution and a little carbolic acid for preservative purposes.

As good results can be obtained with very various proportions of tanniniferous materials and iron salts, it is possible further to multiply recipes for iron inks. Every intelligent maker can soon discover wherein any recipe which he uses is faulty, and a few experiments will then quickly show him what the best proportions are, both as regards the cost and the quality of his ink, of the particular materials which he uses or has at his command.

## X.

## EXTRACT INKS.

The fact that gall-nuts are usually directed in ink recipes as the ingredient for providing the tannin is referable to an old but erroneous idea that they contained a sort of tannin absent from all other vegetable matter. It must be regarded as a great step in advance that we have learned to use other vegetables to prepare inks which are in no way inferior to those made from galls. An ink maker who knows his trade can get his tannin very cheaply indeed, by using some of the materials to be presently named. In the first rank of these are the unripe fruits of the sloe (*Prunus spinosa*), of the bird-cherry (*Prunus padus*), and of the black elder—any fruits, indeed, which have an astringent taste or intense colour.

Most of the barks of our forest trees, also, contain notable quantities of tannin. We may mention specially oaks, pines, elms, and willows. The sumach, the plum, the poplar, the horse-chestnut, and the elder contain tannin in the young twigs as well as in the bark. These vegetable matters also contain extractives which affect the colour of the ink. Some of them give a green ink with ferrous sulphate, some a brown, and many a purple. We seek for ink making purposes such dark colouring matters as will make what the dyers call lakes.

If we add solution of alum to certain vegetable decoctions the colour of the solution changes, and if caustic potash or ammonia is then added we get a precipitate of coloured alumina, which is called a lake. In ink manufacture this lake is not, of course, to be produced in the ink itself. The flocculent precipitate would not remain in suspension. It is a question of having the lake in solution, which is

effected by having free acid present. If we write with an ink so made, we shall see that the writing gradually darkens. The ammonia in the air and the traces of lime in the paper co-operate to precipitate the lake, and thus make the writing more distinct.

The amount of alum to be used can only be known by experience, as it depends upon the nature and the degree of concentration of the decoction. The nature of the decoction depends, too, not only on the plant it was obtained from, but on the age of the plant and the time of year at which it was gathered. When once the right proportion has been hit upon, on adding ferrous sulphate we shall obtain an ink of a particular colour, and we have in indigo-carmine an excellent means of bringing that colour to black, blue, or violet, as may be required. We use gum-arabic or dextrine as a thickening, and add as well a little antiseptic, such as carbolic acid, as these inks are very liable to go mouldy, which must always be particularly guarded against.

Although it is impossible to give recipes for all the substances which can be used for ink making, we give below a sufficient number to act as a guide to the manufacturer.

## Elder Ink.

The berries of the common elder (*Sambucus ebulus*) contain a large quantity of a reddish-blue dye, and give a capital ink. The writing is at first violet, but soon turns to a deep black.

| | |
|---|---|
| Elder berries | 100 |
| Ferrous sulphate | 5 |
| Alum | 2 |
| Vinegar | 5 |

Crush out the juice of the ripe berries and mix it with the vinegar. Then add the alum and the iron salt dissolved in hot water.

### Sloe Ink.

| | |
|---|---|
| Sloes | 200 |
| Ferrous sulphate | 10 |
| Alum | 4 |
| Vinegar | 50 |
| Water | 125 |

Crush the unripe berries and boil them in the water. Strain, and add first the vinegar and then the alum and the vitriol both dissolved in a little hot water. A little carbolic acid is added to all these inks.

### Chestnut Ink.

The prickly shells of the fruits of the horse-chestnut (*Tesculus hypocastanum*) give, with boiling water, an excellent extract for ink making.

| | |
|---|---|
| Green chestnut shells | 400 |
| Ferrous sulphate | 4 |
| Alum | 2 |
| Water | 2,000 |

Boil the shells for a few hours in the water, strain, and add the alum and the vitriol. The bark of the young twigs of the horse-chestnut can also be used instead of the fruit.

### Catechu Ink.

| | |
|---|---|
| Catechu | 10 |
| Ferrous sulphate | 10 |
| Gum | 2 |
| Water | 100 |

Dissolve the cutch in the water boiling, let the solution clear, decant it, and add the iron. In this way a splendid ink can be very quickly made. A few per cent. of strong vinegar is a great improvement.

### Walnut Ink.

The pulp of the fruit of the walnut (*Juglans regia*) contains an extractive which quickly turns brown on exposure to the air, and is sometimes used to dye the skin a deep brown. This pulp gives a very durable ink of a fine black colour.

| | |
|---|---|
| Green walnuts | 200 |
| Ferrous sulphate | 8 |
| Alum | 2 |
| Water | 800 |

## XI.

## LOGWOOD INKS.

Logwood (*Hæmatoxylon campechianum*) contains a colouring matter soluble in water and showing several very characteristic reactions. A decoction or an aqueous infusion made at ordinary temperatures is red, but alkalies turn it blue. The pure colouring matter is called hæmatoxylin, and forms yellow crystals. When the wood is exposed to the air it changes into hæmateine, which is red.

Hæmateine gives a violet compound with ammonia. Treated with solution of alum or lead acetate, and then with ammonia, it gives a blue or violet lake.

The most important property of logwood decoction for our purpose is that of forming very dark liquids with neutral chromates. These liquids can be used as inks or dyes, or for painting. On this account logwood and its extract

are much used by ink makers, and rightly so, for the inks so made have a fine colour, are very durable, and cost little to make.

### English Logwood Ink.

| | |
|---|---|
| Galls | 100 |
| Logwood | 120 |
| Ferrous sulphate | 35 |
| Gum | 100 |
| Vinegar | 400 |
| Water | 500 |

This ink can be got by putting all the ingredients into a vat. Stir every day for about a fortnight. The ink will then be a deep black, and can be bottled. The residue of galls and logwood is then treated with—

| | |
|---|---|
| Ferrous sulphate | 15 |
| Gum | 30 |
| Vinegar | 100 |
| Water | 150 |

and gives a second lot of ink of good second quality. Even a third lot of ink may be got by adding half the quantities last mentioned to the residue after the second ink has been drawn off.

It is, however, a better plan to put the solid ingredients into a bag, which is hung, two-thirds immersed, in the vinegar and water. We thus get an ink that requires no filtering. A wooden ring round the mouth of the bag greatly facilitates the filling and emptying.

The only drawback to this very convenient way of making ink is the liability of the liquid to mould. It is thus advisable to substitute crude pyroligneous acid (which contains carbolic acid) for the vinegar, or if vinegar is used, to add a little carbolic acid.

If it is desired to prepare these inks well in a few hours, the bag should be steeped in the liquid ingredients at the boil, and the galls should be well crushed and the logwood either in the form of extract or of sawdust or very thin shavings.

### French Logwood Ink.

| | |
|---|---|
| Galls | 55 |
| Logwood | 30 |
| Ferrous sulphate | 30 |
| Cupric sulphate | 8 |
| Alum | 2 |
| Gum | 20 |
| Water | 1,500 |

Boil the crushed galls and the logwood shavings in the water till the liquid is evaporated to about half. Then strain boiling, and stir in the gum and the metallic salts in the state of fine powder. The ink is then fit for use, but it is better to allow it to settle a few days. The sediment is put to the residue remaining from the first decoction, and mixed with—

| | |
|---|---|
| Ferrous sulphate | 10 |
| Copper sulphate | 2 |
| Gum | 8 |
| Water | 500 |

Boil for two hours, and strain boiling hot. A second lot of ink is thus obtained, which, although inferior to the first, is better than many common gall inks. It shares with all logwood inks the manifest advantage of containing no free acid, so that it does not injure the nibs. A nib which had been used for this ink till the point had become so worn by friction that it was impossible to make a fine stroke with it appeared, when cleaned with water, perfectly polished, and showed no sign of corrosion.

## Germania Ink.

| | |
|---|---|
| Galls | 200 |
| Logwood extract | 30 |
| Ferrous sulphate | 60 |
| Alum | 4 |
| Vinegar | 10 |
| Carbolic acid | 2 |
| Water | 2,400 |

The powdered galls are mixed with 2,000 of the water, and left in a covered vessel for fourteen days. In the meantime the logwood extract is dissolved in 200 of the water, and the metallic salts in the remaining 200. When the gall infusion is drawn off—it is usually very mouldy—it is mixed with the vinegar and the carbolic acid, and finally with the solution of vitriol and alum. The result is an ink of the very deepest colour, which flows freely and penetrates the paper well. It resists chemicals strongly, and is very suitable for important documents which have to be preserved for long periods.

## Gallic Acid and Logwood Inks.

Although the Germania ink just described is partly a gallic acid ink, as the gall decoction is used in a mouldy state, the process can be also so managed that an ink is obtained which unites the advantages of a good alizarine ink with those of a logwood ink. The following is the recipe for securing this result:—

| | |
|---|---|
| Galls | 200 |
| Ferrous sulphate | 60 |
| Vinegar | 1,600 |
| Carbolic acid | 2 |

The galls are soaked with part of the water and left to ferment for three weeks. At the end of this time all the

quercotannic acid will have become gallic acid. The vinegar is then added, and the liquid is strained. The residue is rinsed with water till the liquid and washings weigh 800. In a part of it we dissolve 40 of logwood extract and 2 of alum, and then put it back to the rest. The addition of the carbolic acid finishes the ink.

As appears from the description, we get first an acid ink, which, if used at that stage, gives pale green writing which gradually turns black in the air. The addition of the logwood makes the ink write a fine blue-black from the first, which soon becomes a deep lustrous black.

All the logwood inks hitherto described have, besides great cheapness of production, the additional advantage that they penetrate the paper very deeply, a circumstance which, of course, greatly increases the durability of the writing. We possess writings executed with them many years ago, some of which have been purposely stored in damp cellars. The writing is as black as ever, while those done with ordinary logwood inks, which have been treated in the same way for the same time, have turned distinctly brown.

## Logwood Chrome Ink.

So far we have described only inks owing their colour to a very finely divided black precipitate suspended in a colourless solution, or those in which the black is in solution in an acid. In reality, however, none of these inks consists of a black solution which would give no sediment on standing. Such a solution, however, exists without any suspended matter whatever. It was discovered by Runge, who found that *neutral* chromates gave with infusion of logwood a very black, clear liquid.

Runge found that the best salt for the purpose was the yellow potassium chromate ($K_2CrO_4$). Although it is not

a rare salt, it is sold at an exorbitant price, and the ink maker who uses it in large quantities will find it advantageous to make it himself by the following process:—

### Preparation of Potassium Chromate.

Dissolve commercial bichromate of potash in ten times its weight of water, boil up, and add powdered carbonate of potash till all effervescence ceases. A slight excess of the carbonate does no harm. The liquid during the process gradually changes from red to yellow. It is then evaporated to about half its bulk in an earthen dish, and then allowed to cool with constant stirring. The chromate then crystallises out in small yellow crystals. The mother liquor is poured off, and the crystals are dried on blotting-paper. The mother liquor can be used instead of water to dissolve a fresh lot of bichromate.

In the bichromate half the chromic acid is less firmly combined than the other half. This seems to be the reason why an ink made with it has the drawback of changing its pure black colour to brown with time, a change probably due to that half of the chromic acid having been set free. If the monochromate is used the black does not change. We do not at present know the nature of the reaction between logwood dye and monochromate. Some chemists think that the chrome combines with the dye. Although we are aware of the existence of various compounds of organic dye stuffs with metallic oxides we do not think there is much foundation for this opinion, for a very small amount of potassium chromate will convert a large quantity of logwood infusion into ink, and the proportion of chrome to hæmateine present is so insignificant that we do not think it likely that there is combination between the two, although it is, of course, possible. We have also found

that the amount of monochromate required to convert a given quantity of infusion into ink varies greatly, probably on account of the variable amounts of colouring matter present in different kinds of logwood. We have also found that it is of great importance to take just the right quantity of chromate. If too little is used the colour is not full enough, and if too much, the black, although satisfactory at first, will turn brown like that got with bichromate. Although it is impossible to give the exact proportions for all kinds of logwood, yet it will be found that a solution of 2 lb. of chromate in 2 gallons of water when added to a decoction of 40 lb. of logwood in 24 gallons of water will always give a satisfactory ink.

The logwood is broken very small, and boiled with the water till the solution is down to 20 gallons. The decoction is then strained, and the chromate solution is added in very small portions, with constant stirring. After a time a sample should be taken. If it is transparent and writes red or violet, more chromate is wanted. Enough has been added when the liquid is black and writes a blue-black. The quantities used and the brand of the logwood should be noted for future reference.

### Logwood Extract Chrome Ink.

It is simpler and better to use the extract than logwood itself.

| | |
|---|---|
| Logwood extract | 2,000 |
| Potassium chromate | 10 |
| Water | 100,000 |

Dissolve the chromate in the water, and hang the extract in a bag in the solution.

These logwood inks are all very cheap, very black, and very durable. They penetrate the paper very deeply, and

after a few days will resist all attempts to destroy them chemically.

### Violet Logwood Ink.

| | |
|---|---|
| Logwood | 100 |
| Alum | 5 |
| Gum | 10 |
| Water | 500 |

Boil the logwood with the water, dissolve the gum in the hot decoction, and finally add the alum previously dissolved in a little hot water. If a more purple shade is desired, reduce the alum to two-thirds or a half of the above quantity. If, however, the ink is to be blue-black with a violet tinge, add carefully a solution of chromate till the wished-for colour is reached.

### Free-Flowing Logwood Ink.

| | |
|---|---|
| Solution of logwood extract | 440 |
| Dextrine | 80 |
| Water | 1,080 |
| Alum | 72 |
| Sulphuric acid | 6 |
| Potassium chromate | 3 |

The sulphuric acid is added before the chromate and the alum.

### Ordinary Logwood Ink.

| | |
|---|---|
| Logwood extract | 1,110 |
| Dextrine | 30 |
| Alum | 600 |
| Water | 80,000 |

To the solution of the extract add first the alum and then the dextrine. The alum is hung in the solution in a bag till it is all dissolved.

### Violet Logwood Ink.

| | |
|---|---|
| Solution of logwood extract | 300 |
| Alum | 12 |
| Dextrine | 15 |

The alum is dissolved by heating it in part of the extract solution. Finally three twenty-fifths of finely powdered acetate of copper is hung in the ink in a bag.

### Red Logwood Ink.

| | |
|---|---|
| Solution of logwood extract | 50,000 |
| Dextrine | 2,500 |
| Alum | 2,500 |
| Acetate of copper | 20 |

The finished ink is carefully reddened with small additions of sulphuric acid, stirring vigorously each time. This ink does not attack steel nibs so much as might have been expected, especially if the ink is allowed to dry on the pen after the first using.

## XII.

## COPYING INKS.

It is unnecessary to enlarge upon the importance of copying inks, especially as we have now succeeded in making copying inks that require no press or any other mechanical contrivance.

The essential feature of a copying ink is to dry slowly, so that the writing may be copied even after a considerable interval. This property is given by mixing the ink with hygroscopic substances, that is to say, such substances as keep moist by absorbing water from the atmosphere. The

hygroscopic bodies which we use are sugar, grape-sugar, dextrine, glycerine, or chloride of calcium. The hygroscopicity of the last substance is so great that it has to be used in very small quantities. Excess of any of these bodies causes the writing to remain too damp and apt to be effaced.

Any of the inks already spoken of can be made into a copying ink by adding to it the proper quantities of thickening and hygroscopic substances, but inks in which there is a suspended precipitate are less suitable for copying inks than those in which the colouring matter is in solution. The reason of this is that the latter inks penetrate the paper more deeply than the former, and hence remain copyable longer than inks in which only the liquid parts penetrate and the coloured precipitate remains upon the surface, where it is only retained by the thickening substance.

A very simple experiment will convince anybody how different the precipitate-containing inks are from the others. The dry writing of one of the former can be washed away in great part with a damp sponge two or three hours afterwards, and even made quite illegible. This is quite impossible when the ink used had its colouring matter in solution.

A copying ink with a suspended colouring matter will generally give one copy only, and that a bad one, while the original will be nearly obliterated. When, on the other hand, a copying ink has its colour in solution, the latter penetrates the paper, and hence the characters consist of liquid of a particular depth. The lowest part of it adheres so to the paper by capillary attraction that it cannot be removed. The surface of the paper may, however, be likened to a soaked sponge, for when another porous body is pressed on to it, it gives up to it part of the liquid it con-

tains, and gives a sharp copy without injuring the original. When the copy is removed there is enough liquid left to give, with a somewhat stronger pressure, a second copy as sharp as the first. By the use of moistened paper and a still greater pressure a third or even a fourth copy can be taken from the same original. The amount of pressure and its duration must be greater for each successive copy, and the pressure is best applied with a copying press.

Before speaking of copying presses we may say a few words about the paper to be used for taking copies. It must be unsized and of a high degree of porosity, so as to suck up the ink freely. It must also be so thin that the copy penetrates it through and through. It is often necessary to hold the copy up to the light before it can be read, especially if it is the third or the fourth copy. These are always pale, even when a very good copying ink is used. It is a good plan to keep the copying paper in a tin box with a cup of water. This will keep it damp, and it will then take more copies than a perfectly dry paper, even with a moderate pressure.

## Copying Presses.

The object of these is to get a uniform pressure all over the paper. To ensure this it is necessary not only to have the original and the copying paper between two unyielding plates, but also between two others having a certain amount of softness and elasticity. Hence the boards of the press consisted in the old forms of strong wooden boards covered with several layers of soft paper. In the newer forms we have iron instead of wood, and the paper coating of the plates is replaced by india-rubber. The use of iron avoids the trouble caused by the warping or splitting of the wood in the old presses.

The old arrangement for applying pressure is a screw,

but the use of a lever is simpler and more convenient. (See Fig. 3.)

The writing to be copied is laid on the lower plate, and covered with the copying paper, and this with blotting-paper. The upper plate is then brought down upon the three. The amount of pressure required depends on three circumstances—the nature of the ink, the time that has elapsed since the original was written, and the degree of dampness of the copying paper. The more deeply the ink of the original has penetrated the paper, the fresher the characters are, and the nearer the paper is to the

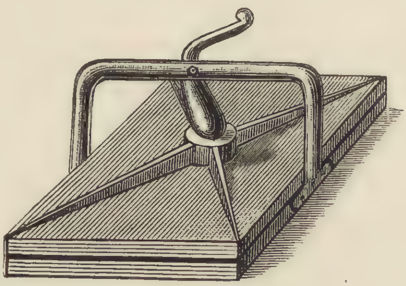

FIG. 3.

right degree of dampness, the less will be the pressure wanted, the sharper the copies and the larger the number of them possible. The pressure causes the copying paper to take up a part of the ink from the original, and the copy is visible on both sides of the paper. Care must be taken in removing the copy, which will, of course, adhere to the original to some extent.

If more copies than one are wanted, the others should be taken as quickly as possible after the first. The longer the time, the more the ink of the original dries and the less distinct does the copy become.

It is possible to obtain copies if the original is damped

on the back by means of a wet sponge long after it has become impracticable to get any without resorting to this device. The wet, of course, soaks through the paper to the ink on the other side and brings it back, at least in part, to the liquid form, when sufficient pressure, after the water has been allowed time to act, will often result in the production of one perfectly good copy at least.

### Copying Books and Skins.

At the present time the copying process has become so simplified that the copying sheets are bound into books containing 500 or 1,000 each. These books are used by placing a skin under the leaf to be used, which is then wetted with a sponge and dried by pressure under blotting-paper till it ceases to shine. The original is then placed on it and covered with a skin. The book is then shut, and a moment's sharp application of the press gives a faultless copy.

The skins are made by soaking white or yellow cartridge paper in fused paraffin. When cold the paper is run through smoothing rolls. It is then quite impervious to water.

### Single Gall Copying Ink.

| | |
|---|---|
| Galls | 120 |
| Ferrous sulphate | 30 |
| Gum | 20 |
| Grape-sugar | 10 |
| Water | 1,000 |

Here the grape-sugar is the hygroscopic agent. As it easily ferments, whereby the ink would be spoiled, some carbolic acid must also be added. If the ink turns out too sticky, mix it with some more which has been made without either gum or grape-sugar.

### Double Gall Copying Ink.

| | |
|---|---|
| Galls | 7 |
| Ferrous sulphate | 7 |
| Logwood | 16 |
| Gum | 5 |
| Grape-sugar | 2 |
| Water | 60 |
| Vinegar | 10 |

The logwood may be replaced by about one-tenth of its weight of logwood extract. A little more does no harm, as it is itself hygroscopic and hence contributes to the copying properties.

### Logwood Copying Ink.

| | |
|---|---|
| Logwood extract | 200 |
| Ferrous sulphate | 4 |
| Copper sulphate | 2 |
| Alum | 24 |
| Grape-sugar | 16 |
| Potassium chromate | 2 |
| Indigo-carmine | 38 |
| Water | 1,000 |

The extract, the indigo-carmine, and the sugar are dissolved in 800 of the water. The other ingredients are dissolved in the rest of the water, and the two solutions are then stirred together.

### Glycerine Copying Ink.

| | |
|---|---|
| Logwood extract | 200 |
| Ferrous sulphate | 8 |
| Potassium chromate | 2 |
| Indigo-carmine | 16 |
| Glycerine | 20 |
| Water | 1,000 |

This excellent ink is made by dissolving the extract, the iron salt, and the chromate simultaneously in the water, and then adding the glycerine and the indigo-carmine. The glycerine does not thicken the ink very much, and the ink flows therefore freely enough for the finest hair-strokes to be made with it. In spite of this great advantage the ink will give many copies, as it dries very slowly and penetrates the paper very deeply.

*N.B.*—It must not be forgotten that in all cases when potassium chromate is included in an ink recipe that salt must be used, and not the bichromate.

### Bottger's Copying Ink.

| | |
|---|---|
| Logwood extract | 64 |
| Carbonate of soda | 16 |
| Potassium chromate | 2 |
| Glycerine | 64 |
| Gum | 16 |
| Water | 270 |

Dissolve the soda and the extract together in the water, then add the gum and the glycerine, and lastly the chromate dissolved in the smallest possible quantity of hot water. The ink is then ready for immediate use. This ink will give three copies merely with the pressure of the hand, and two more afterwards in the press.

### Logwood Copying Ink.

| | |
|---|---|
| Logwood extract | 70 |
| Vinegar | 1,000 |
| Water | 1,000 |
| Ferrous sulphate | 40 |
| Alum | 20 |
| Gum | 35 |
| Sugar | 60 |
| Glycerine | 5 |

### Birmingham Copying Ink.

| | |
|---|---|
| Logwood extract solution | 5,200 |
| Dextrine | 240 |
| Alum | 265 |
| Verdigris | 2 |
| Oxalic acid | 16 |
| Glycerine | 56-168 |

The amount of glycerine used according to the time during which the ink is to remain copyable after writing.

### Allfield's Copying Ink.

This is intended for use without a press. It is made by evaporating 10 gallons of ink down to 6, and then making up to the original volume with glycerine. The copying is done by mere contact of the copying paper, but the copy is very easily smudged.

### Knaffl's Copying Ink.

The following preparation is of the greatest value to architects and engineers, as it gives two or three copies without any wetting of the paper, and of such sharpness that the finest lines of the original are faithfully reproduced. It is rather expensive, but that is of small importance, as its use saves all the great time and labour involved in making a copy of a plan or working drawing by hand.

| | |
|---|---|
| Solution of pyrogallic acid | 240 |
| Copper sulphate | 4 |
| Iron chloride | 10 |
| Uranium acetate | 2 |

Pyrogallic acid is now so much used in photography that it can be bought fairly cheaply. The uranium acetate is dearer, but since uranium compounds have come into use

for black painting on porcelain their price has fallen considerably. The iron chloride is easily made by saturating 10 lb. of commercial hydrochloric acid, adding 1 lb. of strong nitric, and evaporating till crystallisation begins.

To copy a drawing made with this ink a sheet of thick, well-glazed paper is laid on the original (Bristol board answers excellently), and then a smooth board, and the whole is uniformly weighted, but not excessively, with books. In from 3 to 5 days the copy will be ready. Since the invention of hektographs, chromographs, pollymillegraphs, etc., copying inks have lost part of their importance in certain directions. By using these apparatuses with suitable inks we can obtain not merely two or three copies, but 60 or even 100, although with the latter number the last copies are certainly rather pale.

Valuable as the hektograph is when a large number of copies is required, it will never cause the disuse of the ordinary copying process as already described, inasmuch as for business purposes, one copy of a letter or invoice is usually enough, and the somewhat troublesome hektograph process is therefore unnecessary.

## XIII.

## HEKTOGRAPHS.

The consideration of hektography may be divided into three parts—the preparation of the hektograph, the manufacture of the ink, and the making of the copies. These points we now proceed to consider in order.

If a solution of glue which has been boiled down till it would set to a firm mass if allowed to cool is mixed with a certain amount of glycerine, it will then set, indeed, but will remain permanently sticky and very elastic. This

property of a mixture of glue and glycerine has caused it to be used for years for printing rollers.

If we cast the glue-glycerine mass into a flat plate, and write on paper with a very thick-flowing ink containing a very powerful colouring matter such as an aniline dye, either dissolved or in solution, and also glycerine, and then lay the paper, writing downwards, on the gelatine mass with gentle pressure, a large part of the ink will be retained by the gelatine, which will therefore show a reversed copy when the original is taken off. If we then replace the original by a blank sheet of paper, a moderate hand pressure will convert it into an exact copy of the original, and in this way from 60 to 100 copies can be successively obtained. To prepare the gelatine for a fresh writing the old one must be erased with a damp sponge, which removes the upper part of the preparation together with the ink in it. The rest can be used again as soon as it is dry. The "graph" is kept shut up when not in use to prevent its surface from becoming contaminated with dust.

## The Preparation of Hektograph Compositions.

With regard to this very simple matter a whole range of recipes has been published, and all of them give a useable product. A very simple and yet very good method is to take a good quality of size—it is quite superfluous to use gelatine for this purpose—such as gold size, and to soak it in cold water for twenty-four hours. When taken out it will be much swollen, and it is then fused in an enamelled pot over a gentle fire. When all the glue is quite liquid, the glycerine is added and mixed with it perfectly by careful stirring. The mixture is kept hot till it flows thinly, and so that all the bubbles produced by the stirring may rise to the surface and break. Any scum that may rise

is carefully removed with a shallow spoon. The mass is then cast into plates.

The only way to tell whether the preparation is of the right consistency is to take copies with it. If it contains too little water through overheating, and is therefore deficient in elasticity and stickyness, the ink will only give a few copies. It must therefore be mended by stirring hot water into it. If, on the other hand, it has not been evaporated enough, it will be very elastic and so sticky that the paper can only be taken off it with great difficulty, and the copies will smudge and be indistinct. In this case, of course, the mass must be further heated.

Many recipes direct the addition of white powder to the glue and glycerine. The object of these is simply to whiten the mass and make the reversed copy more distinct. They can always be dispensed with.

## Recipes for Hektographs.

### *Simple "Graphs".*

A.

| | |
|---|---|
| Gold size | 100 |
| Glycerine 28 deg. B. | 500 |

B.

| | |
|---|---|
| Gold size | 100 |
| Glycerine 28 deg. B. | 400 |
| Water | 200 |

Mix the size and glycerine as above described.

## Chromographs.

The ink written on a hektograph can be more easily removed when done with if inactive bodies are added in the shape of fine powder. One of the best to use is sulphate of barium. To prepare this, precipitate a solution of

chloride of barium with oil of vitriol, and wash the precipitate repeatedly with water, pouring off each lot of water when the white sulphate has settled to the bottom. The sulphate is used after the last washing in the form of a thin paste.

A.

| | |
|---|---|
| Gold size | 100 grammes |
| Barium paste | ½ litre |
| Dextrine | 100 grammes |
| Glycerine | 1,000-1,200 ,, |

The mass is warmed and stirred till all the size and dextrine are dissolved, and then cast. Test a sample of the mass by copying from it as above directed (p. 70).

B.

| | |
|---|---|
| Gold size | 100 grammes |
| Barium paste | ½ litre |
| Glycerine | 1,200 grammes |

C. (*Recommended by the French Ministry of Public Works.*)

| | |
|---|---|
| Glue | 100 |
| Glycerine | 500 |
| Finely powdered heavy-spar or levigated pipe-clay | 25 |
| Water | 375 |

As ink for this chromograph a concentrated solution of aniline violet is recommended.

In our opinion the simple hektographs are the best. By varying the proportions of size and glycerine we can regulate the number of copies procurable and the ease with which the writing is removed from the gelatine at pleasure.

## XIV.

## HEKTOGRAPH INKS.

As already mentioned the function of a hektograph ink is in the first place to adhere to the composition and to be gradually transferred to the copies. The copies get fainter and fainter until, when the retentive power of the gelatine becomes equal to the absorptive power of the paper, the copying comes to an end, although the writing is still distinct upon the gelatine. One of the first requisites for a hektograph ink evidently is that it should contain a very deep and powerful dye and enough glycerine to make it resemble a very slowly drying copying ink.

Of all known colouring matters the aniline dyes go the farthest, and hence they alone are used in the manufacture of hektograph inks. Those at present in the market are not particularly satisfactory products. They do not flow freely enough for use with the pen. The chief reason of this is that most of the aniline dyes require alcohol to make strong solutions of them, and in use the alcohol evaporates so fast that the ink becomes thick before the pen is empty.

There are, nevertheless, aniline dyes which are sufficiently soluble in water, and among them we have blues and reds which make excellent ink. There is no difficulty in writing with them, and, in fact, only water-soluble anilines should be used for hektograph inks. We can, however, by artifice incorporate anilines which are insoluble in water with the inks with the use of so little spirit that the ink does not dry too fast. The process is as follows:—

The glycerine and dye having been weighed out, the former is heated to about 50 deg. C., and rubbed up with the dye. The coal-tar colours are soluble in glycerine, especially with the aid of heat. If the mass is too tough

to be handled it is diluted with hot water to the consistency of a syrup. When no more solid particles can be felt with the pestle the dye can be brought perfectly into solution by carefully adding about 50 per cent. of spirit. By this method very good hektograph inks can be got even with methyl violet.

## Blue Hektograph Inks.

### *Lehner's Recipe.*

| | |
|---|---|
| Water-soluble blue (Mainz Fabrik) | 10 |
| Glycerine | 10 |
| Water | 50-100 |

Mix with the aid of gentle heat. The amount of water should be taken between the limits stated according to the number of copies required. This ink will be found excellent for every requirement, and to copy the finest strokes perfectly.

## Methyl Violet Inks.

A.

| | |
|---|---|
| Methyl violet | 10 |
| Dilute acetic acid | 5 |
| 90 per cent. spirit | 10 |
| Water | 10 |
| Glycerine | 5 |

B.

| | |
|---|---|
| Methyl violet | 10 |
| Alcohol | 10 |
| Gum | 10 |
| Water | 70 |

The ingredients are kept together for about two hours at 50 to 60 deg. C., and then filtered hot through flannel.

## Red Hektograph Inks.

A.

| | |
|---|---|
| Diamond magenta | 20 |
| Alcohol | 20 |
| Acetic acid | 5 |
| Gum | 20 |
| Water | 140 |

B.

| | |
|---|---|
| Diamond magenta | 10 |
| Alcohol | 10 |
| Glycerine | 10 |
| Water | 50 |

These inks are prepared like those with methyl violet. The second recipe gives a very good ink.

## Violet Hektograph Inks.

Any shade of violet can be got by mixing blue and red inks in different proportions. Specially serviceable in this connection are the blue inks made with water-soluble blue and the red ink last given.

## Green Hektograph Ink.

| | |
|---|---|
| Water-soluble blue | 10 |
| Picric acid | 10 |
| 90 per cent. spirit | 30 |
| Glycerine | 10 |
| Water | 30 |

Different shades can be got by varying the amount of picric acid.

## Black Hektograph Inks.

Aniline black or nigrosine is insoluble in water, and black hektograph inks are got by rubbing up a mixture

of a very dark methyl violet and nigrosine with alcohol and glycerine.

| | |
|---|---|
| Methyl violet | 10 |
| Nigrosine | 20 |
| Alcohol | 60 |
| Glycerine | 30 |
| Gum | 5 |

This ink is always very thick on account of the nigrosine in it being in the solid state. It is therefore little used. We shall return to this important subject when speaking specially of the aniline colours.

## Typewriter Inks.

In a typewriter, when a key is pressed, a lever, on the end of which a letter is cut, is raised, like the hammer of a piano, and, striking an inked ribbon, presses those parts of it which correspond to the relief of the letter on to the paper, which is thus stamped with that particular letter. It is of course necessary that the whole of the ribbon should be soaked with a powerful dye and should retain the proper amount of moisture. It is easy to see then that inks for typewriter ribbons closely resemble hektograph inks, so that this is the proper place to discuss them.

The simplest method of making a typewriter ink is simply to rub up a solid dye in glycerine. We have prepared the following ink in this way, and it has been used for years for typewriter ribbons.

## Lehner's Typewriter Ink.

Heat pure glycerine, and add to it in small portions its own weight of water-soluble blue. On cooling the mass becomes sandy, as part of the dye separates out again in the solid state in the form of minute crystals. Now add

cautiously and with constant stirring just enough water to redissolve these, and no more. The finished ink will then be a thick bluish-black liquid. The ribbon, which is made of thin silk, is run through it, and then subjected to heavy pressure between smooth rollers. In this way a ribbon is got which will give a deep blue writing for many months, even with constant use.

## XV.

## SAFETY INKS.

Chemists have long endeavoured to discover inks which are absolutely indelible except when the material written on is also destroyed. The value that such an ink would have is self-evident. Paper when properly made and kept —in air-tight boxes, for example—is so durable that we do not yet know how long it can last, and documents written on such paper with such an ink would not only resist the tooth of time for thousands of years, but would offer an insuperable barrier to falsification. Unfortunately, there is no known recipe which will yield an ink capable of withstanding all exterior influences. A skilled chemist, who is prepared to devote the necessary time and care to the work, can efface any ink whatever, and leave no trace of its former presence. It is true that free carbon bids defiance to all chemical agents and is insoluble in all our solvents. Ink made with any form of carbon, however, whether lampblack, soot, or charcoal, does not carry the carbon inside the paper. The black particles are simply mechanically attached to the surface, whence they can be perfectly washed off by a skilled hand. Printers' ink alone is an exception. In this important substance lampblack is mixed intimately with boiled oil, which carries the

carbon into the pores of the paper. With very porous paper it is impossible with the greatest skill and patience to efface entirely the characters by any means. Unfortunately printing ink is much too thick to be written with.

Of all the black pigments consisting of carbon, Indian ink contains that element in the most finely divided state. Direct experiments, however, have shown us that even after the lapse of years the writing done with the purest Indian ink can be removed by soaking in water and repeated delicate treatment with a soft sponge. According to our experience the permanence of a writing depends less upon the resisting qualities of the ink than upon the depth to which it penetrates the paper. Hence easily flowing inks used on soft porous paper will give a much more permanent writing than inks owing their colour to solid matter. Ordinary alizarine inks, which contain considerable amounts of indigo-carmine, are very difficult to erase, and when the paper is so porous that the ink penetrates it from side to side its removal is practically impossible.

The inks which consist mainly of vegetable extractives rich in humus are of extraordinary durability. If we write with a solution of grape-sugar mixed with 1 per cent. of caustic potash or soda, the letters are at first a pale brown, but gradually darken, and resist acids or alkalies, and even chlorine, with great energy. The only effect, indeed, of these bodies is to set free more carbon from the humus substances, and so to increase the blackness of the writing.

There are many compositions extolled as safety inks, and some of them are fairly good, but none of them can resist the skill of a trained chemist. We give a few of the best.

### Document Safety Ink.

| | |
|---|---|
| Ruby shellac | 15 |
| Borax | 8 |
| Gum | 8 |
| Soot | 10 |
| Water | 130 |

The shellac is powdered and boiled with the borax and water till dissolved. The solution is filtered. In the meantime the gum and the soot are intimately mixed, put into the vessel in which the shellac was boiled, and boiled with part of the clear filtered solution. When the gum is dissolved the rest of the shellac solution is gradually stirred in. The finished ink is allowed to stand for a few days that the coarser particles of soot may settle to the bottom, and is then decanted or siphoned off.

Shellac-resin forms with the boric acid of the borax compounds of a dark-brown colour, which resist chemical agents so well that the writing cannot be effaced completely without their effects upon the paper being clearly visible. The only object of adding the soot is to make the ink more legible, and the ink is just as permanent without it. It may be replaced by a little indigo-carmine or a very concentrated chrome-logwood ink.

### Read's Safety Ink.

This ink is characterised by its essential constituent being Prussian blue. It is a solution of that pigment in oxalic acid. The purest blue must be chosen, as the inferior qualities are always largely adulterated with chalk and other foreign substances.

In order that the Prussian blue may dissolve readily in the oxalic acid it must undergo a preliminary treatment. This consists in keeping it for a week in an earthen dish

with its own weight of sulphuric acid. The acid is then poured off and the pigment is repeatedly washed by decantation with water until the wash water has no sour taste. When the last lot of wash water has been drained off from the Prussian blue the wet sediment is dissolved in solution of oxalic acid. The usual proportions are 1 lb. of oxalic acid dissolved in 5 lb. of water to every 5 lb. of Prussian blue. The resulting solution is decanted and mixed with its own volume of a good logwood-chrome ink.

Writing executed with this ink penetrates very deep, and is hence very difficult to efface.

### Colophony Safety Ink.

| | |
|---|---|
| Colophony | 10 |
| Soda crystals | 10 |
| Soot | 2 |
| Gum | 4 |
| Water | 100 |

The colophony is dissolved by boiling with the water and the soda. A clear solution is got more quickly if three of the ten of soda crystals are replaced by the same weight of caustic soda. The gum and soot are mixed and stirred into the solution.

### Water-glass Ink.

This is an excellent safety ink. Baudrimont, its discoverer, made it by mixing soot with ten times its weight of silicate of potash. The silicate of potash is bought in the form of a thick solution, which must be kept from the air or it will set solid, by the liberation of silica from it by the carbonic acid of the air. The soot is first mixed with a little of the water-glass by long rubbing, and the paste when quite uniform is stirred into the rest of the silicate. The ink must be bottled up air-tight as soon as

it is made. When it is used the carbonic acid of the air acts upon it as above described, and the silica, enclosing carbon within it, is set free in the pores of the paper. Both the silica and the paper thus protect the carbon from mechanical removal. As, however, the carbonate of potash also formed might injure the paper it should be rinsed out with weak vinegar, which in its turn should be removed by rinsing with water.

## Carbon Safety Ink.

This is a kind of liquid Indian ink prepared from soot.

| | |
|---|---|
| Soot | 10 |
| Gum | 10 |
| Oxalic acid | 5 |
| Water | 200 |

The solid ingredients are rubbed up with the water, which is added to them a little at a time, until a perfectly uniform paste is got which can then be stirred into the rest of the water. This ink, however, and all inks like it, penetrate the paper very slightly. Hence although the carbon they contain enables them to offer successful resistance to attempts to efface them by chemical means, they can be easily and completely removed with care by mechanical processes.

## Vanadium Ink.

This is one of the discoveries of Berzelius. It is prepared simply by adding ammonium vanadate to a filtered decoction of galls. The vanadate is still an expensive salt, and is not purchasable everywhere. It has, however, a far more energetic action than that of potassium chromate or decoction of logwood. A few drops of solution of ammonium vanadate will convert a large quantity of decoction

of galls into a deep black ink, which has the advantage of flowing very freely. The ink cannot be destroyed completely by any known means. The writing always remains readable, and the ink is undoubtedly the best of all safety inks. If vanadium were cheaper it would be extensively used.

### Lehner's Safety Ink.

Mix concentrated sulphuric acid with twenty times its weight of water, and colour the solution with a little indigo-carmine or water-soluble blue. The colouring matter is added merely to make the writing visible from the first. Write with a quill on good paper. In a few days the sulphuric acid will have become strong enough, by the evaporation of the water, to carbonise the paper. As soon as the writing turns black the paper is soaked for a few days in a 5 per cent. solution of carbonate of soda, then rinsed several times with plain water and dried. The black characters will then last as long as the paper itself, and cannot be effaced. If the neutralisation with soda is delayed the paper will be eaten into holes by the acid, but if it is done at the right moment that will not happen.

## XVI.

## INK EXTRACTS AND POWDERS.

Frequent attempts have been made to bring inks upon the market in concentrated forms which would yield a good ink directly they were mixed with water. Although many of these preparations really give good results they are very little used, as writers will not take the trouble of making the solution.

## Ink Extracts.

Ink extracts can be very easily made by evaporating inks to a certain concentration and then bottling them. The process is, however, difficult according to whether the ink owes its colour to dissolved or suspended matter. With the latter kind it is best to concentrate the gall decoction by itself in a shallow pan, but without boiling it, down to about one-quarter of its original volume. The other ingredients are then dissolved in it. The result is a syrupy liquid which gives a good ink with from five to eight times its volume of water.

If an extract for an alizarine ink is wanted the ink is made according to one of the above recipes, and carefully evaporated. For this purpose earthenware vessels should be used, as those of iron or copper are attacked by the acetic acid in the ink. When, too, the ink during evaporation becomes turbid owing to loss of acetic acid, a little of the strong acid should be put in. By observing this precaution and also by evaporating at a low temperature the ink can be got very concentrated indeed, and can then be bottled and diluted with water for use.

Logwood-chrome inks and horse-chestnut inks can be evaporated to very thick syrups without their quality being in the least impaired or the readiness with which the extract gives an ink with water being affected.

## Ink Powders.

These powders make ink when mixed with water. Most inks may be obtained in the form of powder by various simple devices.

## Tannin and Gallic Acid Ink Powders.

The galls, either fermented or unfermented, are extracted with boiling water in the quantities and in the manner directed above. The filtered decoction is carefully evaporated to a syrup. At this stage, constant stirring is begun, and kept up until the contents of the pan are quite dry. The temperature must be kept as low as possible to avoid burning the ink. In the meantime the ferrous sulphate and the gum are made perfectly dry, and are ground together to a fine powder. They are then mixed in the same way with the dry gall decoction. The brown mixture obtained is filled at once into well-stoppered bottles, as it is very hygroscopic. A pinch of this powder converts water in which it is stirred up into ink immediately.

## Logwood-chrome Ink Powder.

This is made by carefully evaporating the ink to dryness, or more simply by finely powdering very dry logwood extract and grinding it up with potassium chromate.

All ink powders should be put on the market and kept in bottles with ground-in stoppers, or in air-tight packets, for although their quality is not deteriorated by the absorption of moisture from the air, they form lumps which are difficult to get out from the receptacles.

## Paper Boxes for Ink Powders.

The following process for making paper boxes which will protect ink powder perfectly from damp can be confidently recommended: Heat paraffin to about the temperature of boiling water, and fill the box and its lid with it, and then pour it out at once. The sides of the box

thus become perfectly air-tight, so that it will keep ink powder quite dry, even in a damp room.

The chief points in the manufacture of ink powder are to keep the temperature of evaporation and drying so low that no burning can possibly happen, and to see that the ingredients are in a state of perfectly uniform mixture. We will now give some recipes which can be depended on for good results.

### Frick's Ink Powder.

| | | |
|---|---|---|
| Gall powder | 42 | All well dried. |
| Ferrous sulphate | 30 | |
| Gum | 15 | |
| Alum | 6 | |

The galls are ground fine with the alum. The gum and the vitriol are powdered separately, and then mixed with the rest. The powder is at once packed or bottled. The ink made by adding this powder to water gives a black sediment, from which it must be decanted. We can nevertheless make an ink powder which is entirely soluble by infusing the galls with water, evaporating the solution to dryness, and grinding up the residue with the other ingredients. The object of the alum in the recipe is to prevent moulding. If it is replaced by boric or salicylic acid, the acid chosen need only be about one-tenth per cent. of the powder.

### Precision Ink Powder.

| | |
|---|---|
| Gall extract | 150 |
| Ferrous sulphate | 25 |
| Copper sulphate | 5 |
| Alum | 10 |
| Gum | 10 |

These ingredients, made absolutely dry and perfectly

mixed together, give a powder which produces with water a very fine black ink of the very highest quality.

### Logwood Ink Powder.

| | |
|---|---|
| Logwood extract | 500 |
| Potassium chromate | 1 |

Make the extract into a syrup with hot water, and stir in the chromate in concentrated solution in hot water. Evaporate to dryness with constant stirring, grind, and pack while still warm.

### Ink Tablets.

Ink tablets are solid masses which dissolve in water, forming ink. The best inks for tablet-making are those in which the colouring matter is in solution. Chrome and horse-chestnut inks answer very well for the purpose. They are made by evaporating the ink to the right point, and then pouring it into tin trays with perpendicular sides about half an inch high. When the mass has set it is cut up with a sharp knife into square pieces, which are wrapped up in tinfoil. To gauge when the ink is sufficiently evaporated let a drop of it fall on a cold iron. If it sets at once to a pasty mass, the ink is ready to be cast. Ink tablets have the advantage that indigo-carmine can be included in their composition, which, on account of the pasty nature of the indigo-carmine, cannot well be done with ink powders.

### Chrome Ink Tablets.

1.

| | |
|---|---|
| Logwood extract | 500 |
| Potassium chromate | 1 |
| Alum | 10 |
| Gum | 20 |

This gives a violet ink. Only as much water is used as is indispensable to obtain a perfect mixture.

2.

| | |
|---|---|
| Logwood extract | 100 |
| Potassium chromate | 1 |
| Gum | 10 |
| Indigo-carmine | 20 |

This gives a beautiful ink. The writing changes from a blue to a deep black.

### Horse-chestnut Ink Tablets.

| | |
|---|---|
| Chestnut extract | 100 |
| Ferrous sulphate | 10 |
| Alum | 2 |
| Gum | 5 |
| Indigo-carmine | 5 |

The extract is made from the green husks of the horse-chestnut or from the young twigs, and evaporated down to the consistency of a paste.

## XVII.

## PRESERVING INKS.

In former days the liability of every ink to mould was accepted with resignation as an unavoidable evil. The visible moulding of an ink is, however, only a symptom, and is attended by many undesirable changes. For example, an ink to which sugar has been added instead of gum to get a lustre often becomes so tough that long threads spin from the nib, and it cannot be written with. This results from the fermentation of the sugar, and can usually be cured by shaking the ink with a freshly pre-

pared gall decoction, and then allowing it to stand. In a short time a tough black precipitate forms, and if the supernatant liquor is decanted it will be a useful black ink.

The fermentation processes which result in the formation of lactic acid have a much more serious effect upon ink, as they gradually destroy the colouring matter. If we find that the ink becomes pale and acquires a strongly acid taste, we may be sure that it will soon be useless. If the process is carried out in time, the ink can be saved by boiling it with some clean iron nails. The ferment is thus killed, and the lactic acid is brought into combination.

When an ink becomes mouldy it gradually gets covered with a green, felty layer of greyish-green fibres, which grow again as fast as they are removed and with such speed that the whole surface will be re-covered in a single night. Even if we throw away the ink and kill the germs adhering to the vessel by boiling it in water, the remedy is only temporary. When the vessel is refilled with fresh ink, it will soon get more germs from the air, and the growth will get as thick as ever, and for a long time no means of combating the evil was known. It was certainly found that an excess of ferrous sulphate had a preservative action, but with the result of increasing the cost of manufacture, and causing the ink gradually to deposit a sediment and to produce characters which quickly turned brown. Additions of alum, too, were found very effectual in preventing mouldiness, but cause the ink to corrode steel nibs, and in the absence of considerable amounts of acid precipitate the colouring matter in the form of an alumina-lake. This not only makes the ink pale, but makes it flow less freely, as may often be noticed in logwood inks containing alum.

It was long since noted that alizarine inks made with

ordinary vinegar were very apt to mould, while those made with pyroligneous acid rarely or never went mouldy. The reason of this certainly rather striking fact is that the pyroligneous acid contains a certain amount of carbolic acid, which is an extremely powerful disinfectant and hence an efficient preventive of mould. It is better to preserve the ink by adding carbolic acid to it than by using pyroligneous acid in its manufacture. Carbolic acid is very cheap, and the ink is perfectly preserved by one-thousandth of its own volume, or even less. The acid possesses, however, a very penetrating odour, which is plainly perceptible even when the acid is highly diluted, and which, as we have reason to know, has brought even very excellent inks into disfavour. We possess, at the present time, another splendid antiseptic which is perfectly odourless, in the shape of salicylic acid. It has no bad effect on human beings, and cannot be too strongly recommended to manufacturers of ink. According to our results it will completely preserve from 5,000 to 10,000 times its weight of ink. A little of it put into the ink-vat will prevent moulding for good and all. The salicylic acid can be added solid or dissolved in a little spirit.

Boric acid is another preservative not less to be recommended. It occurs in the form of mother-of-pearl-like shining crystals, soluble in cold water with some difficulty, but easily in hot. This body, too, will preserve 1,000 times its weight of ink and upwards from mould. The best plan of using it is to hang it in a bag in the ink, so that it will gradually dissolve.

Many antiseptics, the often recommended corrosive sublimate for example, seem to us very ill-suited for ink preserving. Corrosive sublimate in particular is very poisonous as well as expensive, and we have in salicylic acid a completely innocuous and in every way suitable substance,

which, for our purpose, is as powerful an antiseptic as the mercury salt.

Ethereal oils in general, and clove oil in particular, also possess antiseptic properties, and we therefore find the addition of a few cloves or a few drops of the oil to an ink recommended in many recipes. But an ink to which oil of cloves has been added necessarily acquires its smell, which is a disagreeable one to many persons. Besides the preservation by clove oil is only evanescent. In time exposure of the ink to the air resinifies the oil, and it loses its antiseptic power completely.

We thus conclude from a general survey that salicylic and boric acids are the antiseptics which offer the greatest advantages to the ink maker, and which should therefore be universally used.*

## XVIII.

## CHANGES IN INK AND THE RESTORATION OF FADED WRITING.

The preservative agents we have just been discussing have only come into use very recently. We cannot, therefore, form any judgment as to the durability of characters written with inks preserved by their means, and must confine ourselves to considering the behaviour of the ancient inks, which were exclusively iron and tannin inks. Under certain conditions these inks are extremely durable. In a place which is dry and free from ferment spores the writing may remain a full black after the lapse of many centuries, as certain old documents amply prove. These two conditions are, however, very rarely combined. It is very difficult to exclude moisture completely, and even the

* See page 25.

best preserved writings betray the presence of spores under the microscope. These only demand the access of a little more moisture to develop and destroy the writing.

When a writing is destroyed by mould or damp, or by their joint action, the black colour gradually changes to brown, and finally to a pure rust colour. The ink is then entirely destroyed, and nothing remains but basic ferric sulphate. If the paper is then repeatedly wetted through the characters become paler and finally illegible.

When it is a question of restoring the legibility of a faded MS. we must go to work with the greatest care, for unskilful treatment with chemicals may result in the absolute and irremediable destruction of the characters instead of their reproduction. One of the best means of deciphering characters made with an iron ink and which have become illegible, is to convert the iron compounds still adhering to the paper into ferrous sulphide. As this is black, the characters at once reappear. This appearance, however, is only temporary, as the sulphide is oxidised by the air, and the iron returns to the form of basic sulphate. After many attempts we have succeeded in so modifying this process that the letters will remain revived for at least a few days, so that if necessary the document may be copied. We use a cardboard box about 4 in. high, and of length and breadth corresponding to the sheets of paper containing the faded writing. The box has no lid, but can be closed by laying a sheet of glass on the top of it. Half-way up it a frame is placed horizontally, and carries a netting of fine white silk or cotton threads. On the bottom of the box we place two earthen dishes containing yellow ammonium sulphide. We then put in the frame, place the MS. on the netting, and cover the box with its glass lid. The MS. is damped with a sponge before being placed in the box. Care must be taken not to wet the paper too

much, especially if the writing is on both sides, as then the letters are liable to soak through to the other side of the paper. No rubbing is, of course, allowable.

The yellow ammonium sulphide can be bought, or we can make it ourselves by dissolving sulphide of iron (FeS) in dilute sulphuric acid and passing the gas through solution of ammonia until the solution turns yellow. It is then exposed to the light for a few days in a well-stoppered bottle, and turns dark yellow. In a short time after the MS. has been shut up in the box, the letters turn brown, and the colour eventually passes to black. As long as the MS. remains in the box the vapour of the ammonium sulphide will prevent any oxidation of the sulphide of iron, so that the MS. can be copied at leisure. It can also be removed from the box and photographed between glass plates.

In many cases the restoration can be made permanent by the following process:—

The MS. is dipped in a mixture of pure hydrochloric acid with 100 volumes of distilled water. The immersion must be momentary only, so as not to wet the paper below the surface. The hydrochloric acid used must be absolutely free from iron. The paper is then allowed to dry completely in the air, and the writing is then dusted over with finely powdered ferrocyanide of potassium from a pepper-caster, covered with a glass plate and slightly weighted. After a few hours the plate is removed and the paper is dried. The yellow powder is then brushed off. If the paper had the proper amount of moisture when it was sprinkled, the characters will now be distinctly visible and of a blue colour, owing to the formation of Prussian blue by the action of the ferrocyanide on the iron of the ink which has been dissolved by the hydrochloric acid. The paper must now be freed from all traces of hydrochloric

acid, which would in time efface the letters. To this end it is floated for twenty-four hours in a 2 per cent. solution of sodium carbonate crystals, and then rinsed in running water. The restored MS. must be kept in the dark as much as possible, or the light will fade the writing again.

It is much more difficult to restore parchment than paper MSS., for the prepared skin contains substances which produce coloured compounds when subjected to the restorative processes. The process given by Moride consists in soaking the parchment in distilled water until it has swollen up, but all stirring or movement is carefully avoided. When thoroughly swollen, the parchment is drained, and dipped for five seconds in a 1 per cent. solution of oxalic acid in distilled water. It is then dipped in clean water, and then into a 1 per cent. solution of gallic acid. Here it remains until the writing comes out clearly. The parchment is then rinsed with several lots of distilled water, and dried between folds of blotting-paper as quickly as possible.

The oxalic acid makes the iron salt still existing in the bleached ink soluble, so that it can form a fresh lot of black ink with the gallic acid. Unfortunately, the parchment itself often contains so much iron that the gallic acid makes it black all over, when the writing cannot be made out. The same discoloration happens when the parchment is very mouldy, for the gallic acid then turns it brown. Hence it is important to restrict the quantities of chemicals used to the absolute minimum possible, and solutions are used still more dilute than those above given, and the process is repeated with them if necessary. In particular the use of oxalic acid requires the greatest care, for if it acts too long, or in too strong a form, the writing, instead of being restored, will disappear for ever, as the iron of the original ink will pass from the paper into the

solution. If it is a question of restoring valuable documents it is always advisable to experiment with a small portion first. We then find out how the whole will behave, and how far the use of reagents may be carried.

We have tried the experiment of exposing old parchments to the vapour of acetic acid, then letting them dry, and finally spreading them out on a glass and applying solution of gallic acid to the written surface, and have always obtained results at least equal to those achieved by the processes described above. For this process, also, the parchment must first be swollen by soaking in water, or better, by exposure to steam, as long immersion often injures the parchment.

## XIX.

## COLOURED INKS.

Although among writing fluids black inks are the most important, as being those most largely used, there is also a demand from the public for inks of other colours. The origin of this demand is partly a desire to make distinctive appearances in different parts of a MS., and partly fashion and a preference on the part of individuals for coloured rather than for black inks.

In the present state of chemistry it is not difficult to prepare inks of any desired colour. Since the discovery of the coal-tar dyes we have been able to prepare coloured inks very easily by simply dissolving the appropriate dye. All possible colours can, however, be obtained in inks without coal-tar colours, and many of these inks are in great demand. No coloured ink, be it observed, except, perhaps, real indigo-carmine ink, can compete with the black inks as far as durability is concerned. Writings

made with most of them turn pale in a few months, and documents for long keeping should always be written with a good black ink. We proceed to give processes and recipes for making coloured inks, putting inks of the same colour together.

## XX.

## RED INKS.

In the preparation of red inks we generally use redwood. cochineal, or an aniline dye. Magenta can always be had in satisfactory quality, while both redwood and cochineal vary considerably in quality, and require much care in selection. We must therefore describe both of them rather minutely.

### Redwood.

This is also called Brazil or Pernambuco wood. The tree (*Cæsalpinia echinata*) is indigenous to tropical America, especially to Brazil, which indeed owes its name to the appearance of the wood, *brasil* being the Portuguese word for glowing coals. The fresh wood is pink, but changes to a dark red on exposure to the air.

Several sorts are known in commerce. The best and richest in colouring matter is known as Pernambuco wood, after which came Sapan, Jamaica, Braziletto and Bahama woods.

Redwood contains a colouring matter soluble in water, which gives very fine red lakes with alumina or tin. It is therefore much used by dyers and ink makers, although the colour is inferior to those obtainable with cochineal.

## Cochineal.

This colouring matter consists of the dried bodies of an insect which feeds on various cacti, especially the nopal plant. Indigenous to Mexico, both the insect and its food-plants have been acclimatised elsewhere, and nearly all tropical countries now produce quantities of cochineal.

The dried insect appears in the form of silver-grey grains, the nature of which is easily recognised with a lens. The silver-grey sort is the best, and rubs down to a brown powder. The black cochineal is inferior.

Great experience is necessary in buying cochineal, as it is so expensive that the most flagrant adulteration is often met with. A common occurrence is for cochineal from which most of the colouring matter has been exhausted to be resold as fresh goods. In many cases, too, the form of the insect is imitated with flour-paste, and the masses are coloured with a little cochineal and offered for sale.

A simple test of the goodness of cochineal consists in rubbing it up and treating the powder with a little caustic ammonia. If the cochineal is good, a very deep red solution of the dye will be immediately produced.

Before the aniline dyes were known, the finest red inks were those made from cochineal, but those made from anilines now dispute priority with them.

## Redwood Inks.

### *Red Brazil Ink.*

| | |
|---|---|
| Pernambuco wood | 280 |
| Tin salt | 10 |
| Gum | 20 |
| Water | 3,500 |

The wood is boiled in the form of thin shavings with the water in a roomy vessel for about an hour. The decoction is then filtered. The tin salt is dissolved in a little water. If the solution should be turbid from the presence of basic salt, it is cleared by boiling it with a few drops of hydrochloric acid. The gum is now dissolved in the filtered redwood solution, and the tin solution is added. The ink is now finished, unless the colour of the writing with it is too weak, in which case it must be concentrated by evaporation. The tin salt forms a red lake, which remains dissolved unless too much tin is added. If this is the case some of the lake precipitates.

### Pernambuco Ink.

| | |
|---|---|
| Pernambuco wood | 8 |
| Alum | 2 |
| Gum | 2 |
| Water | 60 |

Alumina forms a red lake with redwood, like tin salt. The wood is boiled with the water, and the gum and alum are dissolved in the filtered decoction. If this ink has a violet hue, which is likely to be the case, add powdered tartaric acid to it while it is boiling, putting it in a little at a time, until the desired pure red is produced. After each addition of tartaric acid boil for a few minutes, stir well, and try the colour by writing on paper.

### Brazil Extract Ink.

| | |
|---|---|
| Pernambuco extract | 15 |
| Alum | 3 |
| Tin salt | 2 |
| Tartaric acid | 2 |
| Water | 120 |

Pernambuco wood comes on the market in solid masses

like logwood extract. It gives a beautiful red solution in water which answers as well for ink making as the decoction of the wood, and with the additional advantage of saving much time and trouble. Moreover, the solution can be made so strong that after evaporation of the ink is unnecessary. Although very good, these redwood inks have been almost entirely superseded by cochineal or aniline inks, which are far superior to them in colour.

### Cochineal or Carmine Inks.

Inks can be made direct from cochineal itself, and will be of great beauty and warmth of colour, but for the very best inks the cochineal must first be converted into carmine. The labour of so doing is richly rewarded by the unsurpassable excellence of the resulting ink, and most of the trouble of making the carmine is made up for by the actual preparation of the ink from carmine being easier than from cochineal.

### Preparation of Carmine.

Powder the best silver-grey cochineal as finely as possible, and boil it for three hours in water. Filter the hot solution quickly through a thick linen cloth. Boil up the filtrate again, and add the substances needed to form the lake. Many such substances may be used, but only two can be thoroughly depended upon, and they should both be used together. These two are alum and tin salt, and if necessary warmth may be given to the colour by the cautious addition, drop by drop, of hydrochloric acid. The alum must be absolutely free from iron, or it will be impossible to get more than a very unsatisfactory product. The best proportions are:—

| | |
|---|---|
| Cochineal | 20 |
| Water | 500 |
| Alum | 2 |
| Tin salt | 2 |

The alum and tin salt are added at the boil, which is kept up till everything is dissolved. The clear solution is then exposed in shallow dishes covered with sheets of glass for several weeks in a very bright sunny place. By this time the dark-red liquid will have lost nearly all its colour, and the carmine will have been deposited in the solid form, partly on the dish and partly on the surface of the liquid. It is separated by filtration, and carefully dried with blotting-paper. To get a fine and warm red it is absolutely indispensable that the dishes should get plenty of sun, so that the manufacture is impossible in any but the most favourable weather.

To get absolutely pure carmine, the product already described is dissolved in caustic ammonia. The solution is filtered, and the carmine is reprecipitated with acetic acid. We now give some recipes for carmine inks.

### Best Quality Carmine Ink.

| | |
|---|---|
| Carmine | 4 |
| Caustic ammonia | 500 |
| Gum | 10 |

Pour the ammonia on the carmine and gum, and heat on the water-bath nearly to boiling. Maintain the heat for ten minutes longer, and bottle the solution the moment it is cold, closing the bottles with good sound corks. If the ammonia is allowed to evaporate the carmine will precipitate, as it is insoluble in water. The carmine can, however, be re-solved by adding a little ammonia and shaking.

The solution of carmine in ammonia is sold as soluble

carmine, carmine solution, etc., and is much esteemed for water-colour painting.

It must be remembered that commercial caustic ammonia is not always of the same strength, and that an excess of ammonia makes the carmine solution purple or violet. Hence the ammonia should be added with care. If in spite of every precaution too much is put in, the right colour can be obtained by the very cautious addition of dilute hydrochloric or acetic acid.

### Superfine Cochineal Ink.

| | |
|---|---|
| Cochineal | 40 |
| Carbonate of ammonia | 2 |
| Alum | 2 |
| Water | 200 |

The carbonate of ammonia is dissolved cold in the water, and the solution is poured on to a mixture of the alum and cochineal both finely powdered. Shake every quarter of an hour for 3 or 4 hours. By that time the extraction of the colouring matter of the cochineal will be complete, and nothing remains but to filter the ink.

The alum is required to precipitate from the ink other substances which are extracted from the cochineal together with the colouring matter, and which would otherwise decompose in the ink. When this happens, the ink turns thick and rapidly moulds, at the same time emitting such a disagreeable odour that many persons would throw the ink away long before it became unusable.

### Indelible Silicate-Carmine Ink.

This peculiar compound is made by rubbing up carmine with water-glass solution to a thick paste, to which more water-glass is then added till the ink has the desired colour

and consistency. This ink, which was invented by Bottger, must be kept in well-closed bottles, and only so much must be poured out as is required for immediate use. Exposure to the air makes the ink first gelatinise, then solidify to a glass. This ink is distinguished not only by its beautiful and permanent colour, but by being the most indelible of all red inks. When made of the proper degree of thinness it penetrates deeply into the paper, and can only be removed by caustic alkalies. Even these do not efface it completely.

### Odourless Carmine Ink.

| | |
|---|---|
| Cochineal | 80 |
| Crystallised carbonate of soda | 160 |
| Tartar | 500 |
| Alum | 40 |
| Gum | 80 |
| Water | 1,800 |
| Spirit | 100 |
| or Salicylic acid | 2 |

Dissolve the soda in 1,600 of the water, and soak the cochineal, finely powdered, in the solution for several days, with frequent stirring. The whole is then boiled up, and the alum and the tartar are added in powder. This causes the liquid to froth very much, so that the boiling vessel must be roomy, and the powder must be put in a little at a time. After half an hour's boiling the liquid is filtered, and the remaining 200 of water poured boiling through the residue on the filter. The gum is then dissolved in the total filtrate. The alcohol or salicylic acid is used as a preservative, as the ink is very decomposable. Salicylic acid leaves the ink without smell and unalterable. As this ink is free from poisonous metallic salts it can be used for dyeing confectionery.

### Patent Red Ink.

| | |
|---|---|
| Cochineal | 10 |
| Tin salt | 2 |
| Sal ammoniac | 2 |
| Water | 200 |

The colouring matter is fully extracted from the cochineal by boiling it in the water. While the liquid is still warm it is treated with ammonia and filtered. The filtrate while still warmed is mixed first with the sal ammoniac and then with the tin salt.

### Cheap Cochineal Ink.

| | |
|---|---|
| Pernambuco wood | 60 |
| Tartar | 15 |
| Alum | 15 |
| Gum | 15 |
| Water | 500 |
| Cochineal | 5 |
| Strong spirit | 60 |

Boil the Pernambuco wood with the water for 1½ hour. Then add the tartar and the alum, and boil for another hour and a half. The gum is then added, and then the alcohol with which the cochineal has previously been exhausted by a week's digestion.

If the residual wood is treated with all the other ingredients again, but with one-fourth of the quantity prescribed for each in the above recipe, a fresh lot of ink will be obtained, which can be mixed with the first.

### Purple Ink.

| | |
|---|---|
| Logwood extract | 15 |
| Crystallised verdigris | 10 |
| Alum | 50 |
| Gum | 30 |
| Water | 800 |

The four solids are dissolved separately, and the four solutions are then mixed. Should the shade be too bluish, a few drops of very strong vinegar or of a carmine ink will correct it.

### Carmine Purple Ink.

This is made by carefully adding solution of indigo-carmine to a carmine ink, whereby the pure red of the latter may be changed to violet or purple as required.

### Purple Carthamine Ink.

| | |
|---|---|
| Safflower-carmine | 200 |
| Gum | 750 |
| Cream of tartar | 30 |
| Sugar | 75 |
| Water | 6,000 |
| Carbolic acid | 5 |

### Red Magenta Ink.

Magenta, which is so largely used in dyeing, makes very beautiful red inks. It is sold in green crystals which form a dark-red solution in spirit.

| | |
|---|---|
| Magenta | 2 |
| Gum | 5 |
| Spirit | 10 |
| Water | 100 |

The magenta is dissolved in the spirit, which must be as strong as possible, 90 per cent. at least, with the aid of gentle heat. In the meantime, the gum is dissolved in the water, and the solution is filtered and heated. As soon as it is boiling the magenta solution is poured into it in a thin stream, with constant stirring.

## Eosine Ink.

Eosine is a splendid scarlet dye. Red inks made with it do not surpass the magenta inks in beauty, but have advantages in the brilliance of the written characters. They are made from the crystalline powder, of which commercial eosine consists, exactly in the same way as a magenta ink.

## Coal-Tar Dye Inks in General.

We have coal-tar dyes from which inks may be made of every conceivable colour, in the same way as above directed for magenta ink. Since we have learned to make coal-tar dyes which are readily soluble in water, the manufacture of coloured inks has been vastly simplified. All we have to do is to dissolve the dye in just so much water that the solution shall write of the proper colour. Care must be taken that the solution is not too concentrated, or the writing will have a metallic lustre, and to add enough gum, and also glycerine in the case of a copying ink, to give the right consistency.

The high price of these dyes hardly affects us, as it is compensated for by their enormous intensity of colouring power. In this they so far exceed all other colouring matters that they make remarkably cheap inks. Inks made with coal-tar dyes excel in purity of colour, and can be used with advantage instead of water-colours for retouching photographs, steel engravings, etc. They have also been proposed as colourings for liqueurs and pastry, but although they give very fine colours many of them contain poisonous compounds of arsenic and other metals, and only those which are quite free from metals should be used for colouring articles of food.

# XXI.

## BLUE INKS.

The blue inks which deserve most attention are the solutions of water-soluble blue or indigo-carmine. They are the most deeply coloured, and penetrate so deeply into the paper that they are difficult to efface.

### Indigo-blue Ink.

| | |
|---|---|
| Indigo-carmine | 10 |
| Gum | 5 |
| Water | 50-100 |

First dissolve the gum in water and then the indigo-carmine, and then add more water till the writing is of the proper colour.

### Prussian Blue Inks.

Indigo-blue does not show so well on paper as Prussian blue. This, as sold, is insoluble, and although it can be used as such, does not give such good ink as the soluble Prussian blue. Soluble Prussian blue is also much used as a washing blue, and the ink maker should therefore make it for himself.

### Manufacture of Soluble Prussian Blue.

Mix crude hydrochloric acid with one-tenth of its weight of nitric acid, and then add a weight of distilled water equal to that of the hydrochloric acid. Saturate the mixture with pieces of iron. As soon as it has dissolved as much of the metal as it can, which will take a few days, decant the solution of chloride of iron through a filter.

In the meantime a weight of ferrocyanide of potassium equal to that of the hydrochloric acid has been dissolved in ten times its weight of distilled water, and is now gradually added to the iron solution until no more blue precipitate is formed. No notable excess of either ferrocyanide or chloride should be used. The precipitate is washed several times with water by decantation, and finally filtered off. The paste from the filter is rubbed up with one-tenth of its weight of crystals of oxalic acid, and water gradually added till a clear sky-blue solution is obtained, which can be used at once for ink making.

The trouble of making the iron solution can be avoided by using bought ferrous sulphate, but that salt must first be converted into ferric sulphate by contact for a few days, in solution, with one-tenth of its weight (as a solid) of nitric acid. The solution is then used as above directed for the solution of chloride of iron. In either case, the Prussian blue must not be allowed to dry before treatment with oxalic acid.

If the ink maker buys his Prussian blue he must buy the best, usually called Paris blue, and must prepare it for solution in oxalic acid in a way to be presently described. The bought Prussian blue, being dry, requires far more oxalic acid to dissolve it than it would do had it not been allowed to dry. The result is an ink costing much more to make, and by virtue of the large excess of acid which it contains attacking steel nibs vigorously. To prepare the purchased pigment for solution we mix it with its own weight of concentrated sulphuric acid, and leave it for from 24 to 36 hours in it. We then pour the whole lot into a large excess of water, and wash the precipitate with water by decantation until the wash waters give no blue coloration with solution of potassium ferrocyanide, and are therefore free from iron. The precipitate is then

rubbed up wet with oxalic acid as above described. Under these circumstances the oxalic acid will dissolve six times its own weight of Prussian blue, or eighteen times as much as it will dissolve of the dry commercial pigment.

### Blue Post Ink.

Dissolve 17 of potassium ferrocyanide in 54 of water, and 17 of ferrous sulphate in 1,540 of water. Mix, and treat the blue precipitate with a mixture of—

| | |
|---|---|
| Nitric acid . . . . . . . . . . | 10 |
| Hydrochloric acid . . . . . . . . . | 5 |
| Water . . . . . . . . . . . | 500 |

After 24 hours pour off the liquid, and rub up the precipitate with $3\frac{1}{2}$ of oxalic acid. Then add 4,000 of water containing 160 of white gum in solution.

### Blue Aniline Ink.

Dissolve water-soluble blue in water so that the writing is a good blue without metallic lustre, and thicken with gum. If a copying ink is wanted, add glycerine as well.

## XXII.

## VIOLET INKS.

We now wish to describe some violet inks made differently from those previously discussed. One way of making a violet ink is to mix a red ink with a blue one, and in any case aniline dyes give inks of a much better colour than the violet inks already mentioned. The latter, however, have the advantage of being very cheap.

### Violet Aniline Ink.

This is prepared by dissolving methyl violet in spirit. The alcoholic solution need not be boiled for the necessary dilution with water as is the case with magenta, but the water must nevertheless be added with care. The moment any precipitate begins to appear the addition of water must be stopped, and the liquid made clear again with a little spirit. The necessary amount of gum is then dissolved in the liquid.

The violet aniline inks, although very beautiful, are not particularly durable, and can be easily and completely effaced by chemicals. The following recipe gives a more durable ink:—

### Violet Indigo Ink.

Make a solution of indigo-carmine strong enough to be used as a blue ink, and add to it the proper amount of gum. Then add gradually a very thick solution of carmine, when the ink passes through purple to violet. The ink should be tested from time to time during the making by writing with it. A still finer but less durable ink is made in the same way from solution of Prussian blue and carmine.

### Violet Copying Ink.

1.

| | |
|---|---|
| Glycerine | 10 |
| Oxalic acid | 5 |
| Logwood extract | 40 |
| Alum | 30 |
| Water | 800 |

2.

| | |
|---|---|
| Bichromate of potash | 5 |
| Dissolved in water | 100 |

Make solutions 1 and 2 separately, and then mix them. Boil up the whole then in a copper pan, add 50 of pyroligneous acid, and bottle.

## XXIII.

## YELLOW INKS.

A full yellow ink can be made in several ways, the simplest of which is to dissolve picric acid in hot water. Picric acid is sold in yellow crystals, which are very bitter and poisonous. Picric acid ink must therefore not be used for colouring foods.

### Picric Acid Ink.

| | |
|---|---|
| Picric acid | 10 |
| Gum | 2 |
| Water | 100 |

Boil all together. The water must be distilled water.

### Yellow Gamboge Ink.

Gamboge is a resin which can be emulsified with water, although it will not dissolve. Heat 10 of gamboge in fine powder with 10 of spirit, and then mix it with 5 of gum-arabic first made to a very strong mucilage with water. Then mix with 30 of water.

### Imperial Yellow Ink.

| | |
|---|---|
| Persian berries | 280 |
| Alum | 28 |
| Gum | 36 |
| Water | 1,000 |

Boil the crushed berries with the water for an hour.

Then add the alum and boil another hour. Then filter and dissolve the gum in the hot filtrate.

## XXIV.

## GREEN INKS.

Green, like violet, is a mixture, in this case of blue and yellow. Hence by mixing a blue and a yellow ink in different proportions every imaginable shade of green can be obtained. The best mixtures are picric acid with either indigo-carmine or solution of Prussian blue. The following, however, are some recipes for some green inks which are not mixtures:—

### Klaproth's Green Ink.

| | |
|---|---|
| Crystallised verdigris | 4 |
| Tartar | 2 |
| Water | 16 |

The three ingredients are boiled together, filtered, and bottled.

### Green Chrome Ink.

We are able to prepare from bichromate of potash a green which has not only a lively green colour but is very durable.

| | |
|---|---|
| Bichromate | 10 |
| Hydrochloric acid | 10 |
| Spirit | 10 |
| Gum | 10 |
| Water | 30 |

Mix the bichromate, finely powdered, with the acid, and let it stand for an hour. Into the red solution thus

obtained the spirit is slowly poured, with constant stirring. The reaction is very vigorous, and the liquid froths and gets very hot, and gradually turns to a dark green. If the action gets too violent, a little cold water is put in. To avoid boiling over, it is best to add the spirit in portions, waiting till the frothing after each addition is over before adding the next. The next step is to add carbonate of soda till all effervescence has ceased and a greenish precipitate just begins to form. The liquid is then left covered up for a week, filtered from the salts which have crystallised out, and diluted to the desired colour. Finally the gum is dissolved in it. This ink penetrates the paper deeply, and gives green writing which is absolutely permanent and is very difficult to efface.

### Stein's Green Ink.

1.

| | |
|---|---|
| Indigo-carmine | 120 |
| Gum | 200 |
| Water | 3,000 |

2.

| | |
|---|---|
| Picric acid | 15 |
| Boiling water | 720 |

Make solutions 1 and 2 separately, and then mix them.

## XXV.

## METALLIC INKS.

In ornamental writing it is customary to use inks which produce characters with a metallic colour and lustre. Such inks can be made in two ways. We can either use the metals themselves or certain dyes which, under particular circumstances, acquire a metallic lustre. If an unalterable

metallic ink is wanted, it must be made from a precious metal, gold or silver, for all other metals oxidise in time and change their colour. This is particularly true of copper.

### Real Gold and Silver Inks.

To produce these the metal, in the form of tinfoil, is rubbed up with gum and water in a mortar till even a strong lense shows no sign of metallic lustre. Water is then added, but the ink must be left thick or the metal would rapidly settle to the bottom. As it is, the ink must always be well shaken every time it is used. In the case of gold it is better to dilute with solution of picric acid than with water. Then much more water can be added, and the writing will nevertheless have a fine gold colour and lustre. This use of picric acid lessens, too, the extreme costliness of the ink.

### Copper Ink and Bronze Ink.

These are got in the same way, using the proper foil. The writing turns dull, and in damp places green.

### Imitation Gold Ink.

This is made from aurum musivum, which is rubbed up with a gamboge ink. This ink, although not so beautiful as the real gold ink, has the advantage over bronze ink that it keeps its colour.

### Imitation Silver Ink.

For this tinfoil is rubbed up with the gum, but a better imitation can be made with aluminium foil or filings. The aluminium keeps its silver colour permanently.

### Coloured Inks with a Metallic Lustre.

It is possible to combine any colour whatever with a metallic colour when coal-tar dyes are used. The solution of the dye is thickened with gum, and rubbed up with real or imitation silver, when we get an ink having a metallic lustre and the colour of the dye used. For yellow, red, and brown, we use gold or a golden yellow alloy and a very concentrated alcoholic solution of magenta. The writing is a dark red, and in certain lights shows the green and gold lustre of the crystallised magenta.

We have now exhausted the subject of ink in the narrow sense of the word, but there are other liquids which are applied to special purposes, such as Indian ink, used for perpetuating lead pencil drawings, lithographic and chemical inks, marking inks, and, lastly, sympathetic inks, which are the inks which disappear, or become visible, or change their colour under special treatment. While the sympathetic inks must be reckoned more or less as toys, the remaining kinds just named are widely used, and their manufacture is very remunerative.

## XXVI.

## INDIAN INK.

The Chinese, Japanese, and other Asiatic races write with a brush with a solid ink rubbed up with water like a pigment. This Chinese or Indian ink is remarkable for the durability and lustre of its colour. These properties have caused it to be extensively used by architects and engineers, and in general by people who have to make permanent drawings.

Although we have made enormously greater progress in

chemistry than the Asiatics, they still surpass us so much in the manufacture of certain articles that the imported product always receives the preference over that made in Europe. One of these articles is Indian ink, and the real Asiatic product is always preferred to the European, as it has a deeper black colour and a greater lustre. Most European-made Indian inks are distinctly brown when diluted to any great extent.

We do not know exactly what method of manufacture is adopted in China. There are reports, which, however, cannot be regarded as very reliable, that the process consists in burning certain plants in a limited supply of air, and passing the smoke through very long paper tubes. The soot deposited in those parts of the tubes which are farthest from the fire, *i.e.*, the finest particles, is selected for making the ink. Other accounts say that the smoke used is got principally by burning sesame oil. This is so burnt in lamps that it gives a very smoky flame. It appears to us not impossible that a product which is manufactured over such an extensive area may be made from various raw materials and in various ways.

When we examine real Indian ink we find that it consists mainly of carbon in a state of excessively fine subdivision, with a binding material probably consisting of gum, but also containing camphor (up to 2 per cent.) and musk. The special smell of real Indian ink is certainly due to the presence of musk, of which only very minute quantities are needed to produce it.

The points to be noticed in real Indian ink are two in number. The carbon is pure, *i.e.*, free from tarry matter, and is in a state of extraordinarily fine subdivision. Now we have devised a process by which such carbon can be prepared without much difficulty. We burn a fuel rich in carbon, such as petroleum or purified oil of turpentine, in

lamps with a feeble supply of air. The smoke is passed through a zinc tube at least 100 feet long, and with a slight upward inclination from the lamp, so as to produce the necessary weak draught. The soot which accumulates in the parts of the tube near the lamps can be used with advantage for articles less expensive than Indian ink. It makes excellent printers' ink for example. That which is gathered from the most remote part of the tube is quite fit for the finest Indian ink, after it has been purified from the traces of tarry matter which adhere to it, and which impart the brown colour to inferior inks. This purification is effected by making the soot into a thick paste with nitric acid by means of a glass or porcelain spatula. This is then made to the consistency of honey by adding a little distilled water. The mass is then heated in a porcelain basin till thick fumes of nitric acid are evolved. In this way a large part of the tarry matter is completely destroyed, and moreover produces finely divided carbon by its destruction. The mass is now largely diluted with water, and allowed to settle. The dilute acid is then poured off, and the washing with water is once repeated. The sediment is next boiled for half an hour with a strong solution of caustic soda. This destroys the rest of the tarry matter, and the carbon left, after repeated washing with water, is in a state of the finest possible subdivision and practically chemically pure. It is then dried in vessels covered to keep out dust, and made into a paste with clear solution of gum. This paste is thickened by stirring and heating till it sets quite hard on cooling. Just after it has been removed from the source of heat a little tincture of musk is stirred into it. The mass must then be cooled slowly in a warm place. When it begins to crack it is kneaded into a lump which is rolled out into a flat plate and dried further till it can be cut into the usual

quadrangular sticks, and will take a clean impression of a stamp. The sticks are formed in metal moulds, having Chinese characters on the inside and representations of dragons, etc. The overflow from the moulds is cut off with a sharp knife, and the rods are ejected by inverting the mould and tapping it. Then they are perfectly dried, and, if wished, wrapped partly or entirely in gold or silver leaf. If any cracks appear in them, these are filled with fresh paste and smoothed over. The pieces must be hard, have a lustrous pure black surface, and show a perfectly uniform and compact fracture.

Indian ink prepared as above directed and in which care has been bestowed on the moulding as well as on the manufacture cannot be distinguished from the Asiatic-made article, even by experts. In uniformity, colour, and lustre it yields to no Chinese manufacture, and surpasses some genuine Indian inks.

A somewhat inferior article can be made from ordinary soot by boiling it with caustic soda lye, washing, and mixing with gum as above directed, and then moulding the paste in the usual way.

## XXVII.

## LITHOGRAPHIC INKS AND PENCILS.

Lithographers require special inks or pencils, according to the particular method of procedure. If the stone is polished the drawing is executed in lithographic ink on it with a pen or brush. When the stone is then treated with a dilute acid the ink protects the parts it covers, which therefore become raised above the etched part of the stone, and the sheets can then be printed from it. When, however, MS. is to be reproduced by lithography the MS. is written

on prepared paper with lithographic copying ink. The paper is then laid, writing downwards, on the smooth stone, and the ink is transferred to the stone by pressure. The acid is then used as before.

When the lithography has to be done on a rough stone, pencils and solid ink are employed.

The inks and pencils used for lithography must always contain acid-resisting bodies, and must be capable of giving a number of impressions. Such bodies are fat, rosin, and wax when converted into a soap.

### Lithographic Ink.

| | |
|---|---|
| Water | 140 |
| Gum lac | 100 |
| Mastic | 30 |
| Rosin | 10 |
| Tallow soap | 70 |
| Soot | 32 |

To use this recipe we require a copper boiler with a lid and a copper pan with a spout. We first melt together all the ingredients, except the wax, in the pan, and get a uniform mixture by thorough stirring. The wax is heated by itself in the larger vessel until it can be ignited. This is then done, and the contents of the pan are stirred into the burning wax. As soon as all the ingredients are in the boiler, the wax is put out by putting on the lid, and the heat is moderated till the mass only keeps in fusion. It is then ladled out into metal moulds which give it the same shape as the rods of Indian ink.

This ink is written with after rubbing up with warm water, just like Indian ink. Any ink rubbed up which is to be left overnight should be covered up to keep it moist, for if it has to be rubbed up again it will very likely form

lumps which will spoil the work, more particularly if a brush is used.

It has been recommended to dissolve the ink in hot water and bottle it. Although this saves constant rubbing up, the practice is not good, as the rubbing up each time gives a more uniform and reliable writing liquid.

### French Lithographic Ink.

| | |
|---|---|
| Shellac | 30 |
| Mastic | 6 |
| Carbonate of potash | 6 |
| Hard tallow soap | 6 |
| Soot | 2 |

Melt the soap with the shellac and the mastic, and stir the carbonate and the soot into the fused mass. As soon as the mixture is uniform it is cast in the moulds.

### Vienna Lithographic Ink.

| | |
|---|---|
| Wax | 18 |
| Soap | 18 |
| Shellac | 14 |
| Rosin | 6 |
| Tallow | 10 |
| India-rubber | 2 |
| Oil of turpentine | 5 |
| Lampblack | 6 |

Fuse the first five ingredients together, and heat till the mass begins to bubble. Then stir in the lampblack and also the india-rubber, previously dissolved in the turpentine. When the smell of the turpentine has nearly disappeared cast the mass into sticks.

### Munich Lithographic Ink.

| | |
|---|---|
| Wax | 20 |
| Tallow | 10 |
| Shellac | 20 |
| Soap | 20 |
| Carbonate of soda | 30 |
| Soot | 10 |

Fuse all together at a strong heat, and stir thoroughly.

### English Lithographic Ink.

| | |
|---|---|
| Virgin wax | 12 |
| Tallow | 12 |
| Hard tallow soap | 12 |
| Shellac | 24 |
| Mastic | 16 |
| Venice turpentine | 2 |
| Lampblack | 22 |

Heat the turpentine, and add to it the shellac, the mastic (both finely powdered), the tallow, the wax, and the soap in the order named. Finally mix in the lampblack intimately. The tough mass produced on cooling is rolled out and cut up and shaped.

### Lithographic Chalk.

This is used for drawing on the stone. It must be dense enough to take a sharp point without breaking, like a good lead pencil, and give a uniform stroke with a light pressure.

### London Lithographic Chalk.

| | |
|---|---|
| Wax | 30 |
| Tallow | 25 |
| Soap | 20 |
| Shellac | 15 |
| Lampblack | 6 |

Fuse all together, and heat till the mass can be set fire to. It is then allowed to burn for a time, which requires some experience to judge it. The condition of the mass can, however, be judged of at any time by extinguishing it by putting the cover on the boiler, and then making a stick of the mixture and trying how it will write. If the stick will not bear a sharp point, having some elasticity and writing a uniform black line, the mass in the boiler must be set fire to again, and again tested a few minutes later. The finished mass is rolled out on a hard surface, and made into pencils the thickness of a goose quill and about 3 in. long.

### French Lithographic Ink.

| | |
|---|---|
| Tallow | 100 |
| Soap | 85 |
| Shellac | 70 |
| Mastic | 10 |
| Lampblack | 10 |

Fuse together and ignite, and proceed altogether as directed under the last recipe.

### Autographic Inks.

These are intended for transferring a writing or drawing to the stone, so that the latter can be printed from directly it has been etched. Here we have a means of securing a number of copies, which is very important for circulars, letters, plans, etc.

It is undeniable that certain difficulties attend the preparation of these inks, for it is necessary to prepare a liquid which, besides possessing the properties of an ordinary ink, will cling fast to the stone and give copies for a considerable time. The paper used may be any usual paper, provided it is not too rough, for common work

such as a circular, but if fine work is necessary, as in preparing copies of a pen and ink drawing or of an architect's plan, prepared paper only is usable.

## Preparation of the Paper.

By following strictly the recipe about to be given the finest line or point can be faultlessly reproduced in the copies. The stone can be etched immediately the transfer has been made, and many thousands of good copies can be printed off.

A fine, strong, unsized printing paper is spread out on a smooth board, and poured over first with a 10 per cent. solution of gelatine. The board is then tilted and the gelatine run off, and a 5 per cent. solution of tannin is next poured on. The paper is again drained and dried. The two processes and the drying are then repeated a second or a third time, and the paper is finally calendered. This paper will not only transfer as above stated the finest lines of a drawing, but will also take the minutest details of a copper or steel plate, and transfer them to the stone.

When the drawing or writing has been laid on the stone the two must be forcibly pressed together several times. The paper is then carefully taken off. The repetition of the pressure is made necessary by the fact that the stone takes an appreciable time to take the ink so strongly that it will not be affected by the etching.

## Best Autograph Ink.

| | |
|---|---|
| Wax | 110 |
| Tallow | 30 |
| Soap | 110 |
| Shellac | 50 |
| Mastic | 40 |
| Rosin | 10 |
| Soot | 30 |

These are fused together in an iron vessel, and the temperature is then raised until disagreeable vapours are largely produced. The mass is then cast into moulds or rolled into cylinders.

The autographic inks can also be used very well for ordinary writings with a steel pen, so long as the letters are not too small.

### Autographic Drawing Copying Ink.

*Ground Mass.*

| | |
|---|---|
| Wax | 70 |
| Tallow | 75 |
| Soap | 60 |
| Copal | 45 |
| Shellac | 70 |
| Mastic | 70 |
| Pitch | 10 |
| Linseed oil | 10 |
| Sulphur powder | 10 |

The copal is first fused with the linseed oil, and so strongly heated that thick, strong-smelling fumes appear. The soap is then added, then the tallow, then the wax, and then the other resins. The whole is next strongly heated and set fire to. During the combustion the sulphur is sprinkled on to the mass, which is continually stirred. The combustion must be maintained until about three quarters of the mass has been burnt away. The fire is then put out by covering the vessel with its lid.

### Autographic Ink No. 1.

| | |
|---|---|
| Ground mass | 12 |
| Distilled water | 100 |
| Indigo-carmine | 5 |

The ground mass is boiled with the water till the liquid

is reduced to one half. The clear brown liquor is then poured off, and the indigo-carmine is dissolved in it. The ink is then bottled.

If the ground mass has not burnt long enough the ink will not copy well, as it will dry too quickly. If, on the other hand, the combustion has been unduly prolonged, the ink will not adhere properly to the stone. It must also be remarked that when the writing is transferred to the stone, the back of the paper must be well damped to facilitate the transfer of the ink from it to the stone.

### Autographic Ink No. 2.

| | |
|---|---|
| Wax | 200 |
| Soap | 60 |
| Tallow | 32 |
| Shellac | 16 |
| Black pitch | 8 |
| Lampblack | 40 |

The ingredients are all fused together and stirred to a uniform mixture, which is gradually heated till it fumes strongly. As soon, however, as the mass catches fire the cover of the vessel is put on, as the burning must not be allowed to continue. The finished ink is then cast into sticks, and for use is rubbed up with warm water.

### Autographic Ink (Andés).

1.

| | |
|---|---|
| Shellac | 6 |
| Wax | 2 |
| Fat | 14 |
| Mastic | 8 |
| Soap | 6 |
| Soot | 2 |

2.

| | |
|---|---|
| Refined mutton tallow | 100 |
| Yellow wax | 125 |
| Soap | 16 |
| Shellac | 150 |
| Mastic | 125 |
| Turpentine | 16 |
| Soot | 30 |

3.

| | |
|---|---|
| Soap | 100 |
| Wax | 118 |
| Fat | 50 |
| Mastic | 50 |
| Soot | 30 |

4.

| | |
|---|---|
| Wax | 6 |
| Mutton tallow | 11 |
| Soap | 12 |
| Shellac | 11 |
| Mastic | 90 |
| Venice turpentine | 2 |
| Soot | 20 |

## Carbon Papers.

These are used for producing a copy of a writing while the writing is being executed. To prepare them, strong, smooth paper is covered on one side with an intimate mixture of yellow wax and an equal weight of the finest Paris blue with ten times the weight of purified tallow. The mixture is well fused and stirred, and is applied to the paper hot. The prepared paper is laid between two unprepared sheets, and the sheet which is in contact with the uncoated side of the prepared paper is written on with a blunt pencil, whereby the writing is copied on the lowest sheet as it is made on the uppermost one.

## Photographic Copying of Drawings.

Certain chemical compounds are altered by light, and can therefore be used for copying writings or drawings made on one side only of the paper by photography. We will describe the process known as Cyanotypy, which consists in soaking paper in the dark-room with a solution of 10 oz. of ferric chloride and 5 oz. of tartaric acid in 100 oz. of water, or with a solution of 10 oz. of ammonia-citrate of iron and 10 oz. of potassium ferricyanide in 60 oz. of water. The paper is then dried and exposed to the sun for an hour under the copy. The paper is then developed with a 10 per cent. solution of ferrocyanide of potassium, thoroughly rinsed and dried. The writing, etc., will then show white on a blue ground.

## Copying Process for Indian Ink Drawings and Engravings on Copper or Wood.

Dissolve oxalic acid in cold water, boil up, and add as much molybdic acid as the boiling solution will dissolve. The solution is then kept in bottles of black glass. Paper is soaked with this, and then dried in the dark-room, and then exposed under the photograph, drawing or engraving in an ordinary printing-frame. The copy is then obtained white on a dark-blue ground. If the paper of the engraving, etc., is very thick, the passage of light through it must be facilitated by lightly rubbing it on the back with petroleum.

## XXVIII.

## INK PENCILS.

It is unnecessary to enlarge on the usefulness of these articles, which combine the convenience in use of a lead pencil with the production of ink-writing with its special appearance and durability. The manufacture of ink pencils has received a great impulse from the discovery of the coal-tar colours, but although many makers put them on the market, certain faults have restricted their use within somewhat narrow limits. They are either too soft, so that they absorb water from the air and make smudgy writing, or so hard and brittle that they break whenever any attempt is made to sharpen them. The question is one well worthy of the attention of manufacturers, and we proceed to give some recipes. The prime conditions of making a really usable ink pencil are to have the ingredients in a state of the finest possible subdivision, and to bring them into sufficiently dense rods by high pressure. We consider that it is advisable to cover the point when the pencil is not in use by a metal cap, and to keep the paper to be used in a damp place. The characters then come out strongly, with gentle pressure on the point of the pencil. The aniline dyes which should be used are magenta for red, water-soluble blue and methyl violet for their respective colours, and nigrosine for black.

### Faber's Ink Pencils.

| | Aniline Dye. | Graphite. | Kaolin. |
|---|---|---|---|
| 1. | 100 | 75 | 25 |
| 2. | 46 | 34 | 24 |
| 3. | 30 | 30 | 40 |
| 4. | 25 | 24 | 50 |

The three ingredients are thoroughly mixed, and the mixture is then forced through holes in a plate, so as to form it into rods, which are finally dried. No. 1 is very soft, No. 4 very hard.

According to another recipe 10 lb. of best logwood are boiled with 100 lb. of water. The decoction is evaporated down to 100 lb., and a solution of chromium nitrite is added till the precipitate at first formed has redissolved to a bluish-black liquid. This is evaporated on the water-bath till it can be formed into rods, after being mixed with from 3 to 4 times its weight of fat-clay and solution of gum-tragacanth. This recipe seems to us faulty, and gives results very inferior to those obtained with the aniline dyes.

## Pencils for Writing on Glass, Porcelain and Metal.

The ingredients are thoroughly mixed, and shaped into sticks by hydraulic pressure. The sticks are then encased in wood like pencil-leads. Their use requires a fair amount of pressure, but the writing cannot be washed away with water.

1. *Black.*

| | |
|---|---|
| Soot | 10 |
| Wax | 40 |
| Tallow | 10 |

2. *White.*

| | |
|---|---|
| Chalk | 40 |
| Wax | 20 |
| Tallow | 10 |

3. *Pale Blue.*

| | |
|---|---|
| Prussian blue | 10 |
| Wax | 20 |
| Tallow | 10 |

4. *Dark Blue.*

| | |
|---|---|
| Prussian blue | 15 |
| Gum | 5 |
| Tallow | 10 |

5. *Red.*

| | |
|---|---|
| Cinnabar | 20 |
| Wax | 60 |
| Tallow | 20 |

6. *Yellow.*

| | |
|---|---|
| Chrome yellow | 10 |
| Wax | 20 |
| Tallow | 10 |

## Pencils for Writing on Glass.

1.

| | |
|---|---|
| Water | 16 |
| Red lead | 8 |
| Tallow | 2-4 |

The ingredients are thoroughly mixed and fused together, and cast into sticks. The variation in the amount of tallow enables the pencils to be made harder or softer.

2.

| | |
|---|---|
| Tallow | 5 |
| Wax | 10 |
| Tallow soap | 10 |
| Red lead | 10 |

The red lead is stirred in after the other three ingredients have been fused together. The mass is shaped into cylinders before it is quite cold, after having been stirred to the last possible moment. The sticks tend to become brittle with age, and should therefore be kept in a warm place.

## XXIX.

## MARKING INKS.

These are the inks used for writing on garments. It goes without saying that they must resist washing, and must be capable of immersion for weeks on end without change. They have, however, to resist also the various substances used in laundries. It is often required of them in addition that they should be still distinctly visible when the place marked has been dyed and then bleached again.

Only a few substances are known which answer fully all the requirements made in respect of a marking ink, and only those which depend for their colouring matter on free carbon are absolutely indelible.

Solutions of the precious metals, gold, silver, platinum, and iridium (a rare metal closely allied to platinum), have the property of being decomposed by organic matter, the metal being separated out in an extremely finely divided state, and forming a very distinct writing.

Silver compounds are decomposed by light alone, and turn black by the separation of very finely divided metallic silver. This circumstance, as well as the fact that silver is the cheapest of the precious metals, makes silver the most suitable for metal marking ink. (Gold is fifteen times the price of silver, and platinum seven times.) We know, however, organic dyes which can be brought into a form in which they are soaked up by a fabric, and form with it insoluble compounds. Such a substance, for example, is indigo-white, which is almost entirely indelible on animal fabrics such as wool and silk. The organic marking inks have here a great advantage over those prepared from metals, for writings made with any metallic salt can be

eradicated without leaving any trace and with comparative ease. Silver can be removed by solution of cyanide of potassium, and gold and platinum by chlorine water. Writings done with indigo-white and carbon, on the other hand, are practically indestructible, for even after the indigo has been got rid of the carbon adheres to the fibres with such tenacity that it cannot be removed without radically injuring the fabric.

## Metallic Marking Inks.

### A.—Silver Inks.

There is a large number of recipes for marking inks of which the basis is silver, and we shall presently give the more important of them. In all cases without exception the salt of silver used is the nitrate. On account of the price of this salt, those who use it in anything like large quantities should make it for themselves, especially as it can be done very easily.

#### *Preparation of Silver Nitrate.*

The first condition of suitability for marking inks of nitrate of silver is freedom from copper, and a perfectly pure salt can be got as follows:—

Pour nitric acid over some silver in a glass vessel. The metal dissolves rapidly with evolution of suffocating fumes of nitrous acid. The solution obtained will be more or less blue, according to the amount of copper present. It is diluted with distilled water and precipitated with hydrochloric acid. The white, curdy precipitate settles quickly, and when the further addition of hydrochloric acid produces no more of it the supernatant liquid is decanted through a filter, on to which the precipitate is received. Here it is washed with distilled water until the filtrate gives no blue

colour with ammonia, a sign that all the copper has been washed away.

The precipitate is then put, together with strips of zinc, into somewhat dilute hydrochloric acid. The colour of the chloride of silver soon changes to a peculiar metallic grey as it becomes reduced to the metallic state. After some days the mass is filtered off, and the pure silver on the filter is washed with distilled water until a sample of the filtrate remains perfectly clear on the addition of ammonia. The silver is then dissolved in nitric acid, which must be free from hydrochloric acid, or some of the silver will return to the state of chloride and remain undissolved. The solution is then evaporated down, but is not allowed to boil for fear of loss by spirting. As soon as the contents of the dish are solid the heat is raised till the salt fuses, and then immediately removed. We shall then get the nitrate of silver in the form of a colourless crystalline mass. It gradually blackens when exposed to the light, and should be kept in the dark or in orange-coloured bottles. It should leave no residue on solution in water.

A simpler method of preparation is to dissolve the impure silver-containing copper in pure nitric acid, evaporate the solution down, and heat the residue. This then turns dark and evolves fumes of nitrous acid, for the nitrate of copper decomposes at a lower temperature than the nitrate of silver into nitrous fumes and black oxide of copper. The secret of success in this method is therefore to work with such a temperature that the nitrate of copper is decomposed, but not the nitrate of silver. The process is regulated by occasionally taking a sample of the fused mass on the sharp point of a glass rod. This sample is dissolved in water and tested with ammonia. As soon as this ceases to produce a blue colour the decomposition of the copper salt is complete, and the mass is at once allowed

to cool. The grey solid then obtained consists of nitrate of silver mixed with finely divided cupric oxide, which is removed by dissolving the nitrate of silver in distilled water and filtering off the solution for use.

Whichever of these two methods of preparing silver nitrate is adopted, it is necessary to fuse the salt obtained to get rid of the last traces of the nitric acid, which would otherwise damage the fabric by passing into the marking ink.

### *Preparation of the Fabric for Marking.*

It is, of course, possible to write with a mere solution of nitrate of silver, but the writing will then run, and will, besides, not adhere strongly to the fibre. But if the fabric, whether linen, cotton, silk, or wool, is first prepared at the spot to be marked, we can use the plain nitrate of silver as a marking ink, either with the pen or with a rubber stamp, and get perfectly sharp letters. We dissolve equal weights of soda crystals and gum-arabic in a weight of water equal to ten times the weight of either, and filter the solution. The place to be marked is soaked with this solution and dried, and when quite dry smoothed with a hot iron. The solution of nitrate of silver being colourless it must be coloured with some inactive colouring matter to make the writing visible from the first.

### *Silver Marking Ink.*

| | |
|---|---|
| Nitrate of silver | 4 |
| Water | 40 |
| Gum | 4 |
| Soot | 2 |

Dissolve the gum by itself in half the water, and rub the solution carefully with the soot. Then dissolve the

silver salt in the rest of the water, and mix the two lots by thorough shaking. Other indifferent colouring matters may be substituted for the soot, *e.g.*, finely powdered indigo or a solution of sap green, or of any soluble aniline dye, such as water-soluble blue, taking in each case only enough to make the writing legible from the first.

When the marking is done it is left exposed to the light, if possible to the direct rays of the sun, when the writing blackens by the formation of metallic silver. The nitric acid which is set free at the same time is neutralised by the soda used in preparing the fabric. If this preparation has been omitted, delicate fabrics would be worn into holes by the acid. As soon as the writing ceases to darken, the marked place is rinsed in warm, soft water. After that the garment may be washed in the ordinary way without injury to the marking.

It must be remarked that steel pens must not be used with metallic marking inks or the silver will be precipitated on the nib, some of the steel of which will dissolve to take its place. Not only do the marked letters thus become paler, but often acquire a rusty edging due to the presence of oxide of iron. A quill should always be used. It will be blackened the first time it is used with a silver ink, and browned with a gold ink, but subsequent employment of the same pen will not entail any further loss to the ink, especially if the pen is rinsed in soft water each time it is used.

### *Ammoniacal Silver Ink.*

If caustic ammonia is added to a solution of nitrate of silver in water, a precipitate of silver oxide is at first formed, but soon dissolves if more ammonia is added. In this way we get a solution which always remains clear and deposits no sediment, while the non-ammoniacal silver

inks always give a black deposit of silver on keeping, and thus gradually become so weak as to be useless.

*Normal Ammoniacal Silver Ink.*

| | |
|---|---|
| Nitrate of silver | 6 |
| Gum-arabic | 6 |
| Soda | 8 |
| Distilled water | 15 |
| Ammonia | 12 |

Dissolve the nitrate in the water in a stoppered bottle, then add the ammonia, and finally the gum and the soda. The bottle is then heated in hot water till the colour of the liquid is so dark that it will write legibly. The stopper is left out during the heating. Care must be taken not to overheat, or so much ammonia will be lost that the ink will precipitate. For the same reason the finished ink must be kept well stoppered up, and must also on account of the action of light on silver inks and metallic inks in general be kept in the dark. The foregoing ink is particularly suitable for writing and drawing with the pen. If it flows too thinly, add more gum to it.

*Silver Stamping Ink.*

| | |
|---|---|
| Nitrate of silver | 10 |
| Ammonia | 20 |
| Soda | 20 |
| Gum | 25 |
| Water | 80 |

Dissolve the silver in the ammonia, and the soda and gum in the water. Then mix the two solutions, and heat till the at first turbid liquid becomes perfectly clear and of a fine brown colour. For use with the pen the ink is now ready, but for use with a stamp the amount of water used should be less, so that the ink may be thicker and give sharp letters with the stamp.

For large establishments where the weekly washing is heavy, such as hotels, hospitals, etc., there is no better marking ink than this. With the stamp especially, it gives the finest lines and details with great distinctness and durability with a very moderate amount of pressure.

### *Cheap Silver Ink.*

The silver inks already given are somewhat dear, as the nitrate of silver must be used in the form of concentrated solution in order to get a deep black writing. But if we combine the silver salt with copper salts a dark black can be got without much silver.

When ammonia is added to a solution of a copper salt we get first a pale blue precipitate of hydrated oxide of copper, which dissolves in an excess of ammonia, forming a magnificent dark-blue solution of cuprate of ammonia. If writing executed with this ink is heated, say with a flat iron, a deep black results from the formation of black oxide of copper.

Hence, if we make ink of a mixture of argentate and cuprate of ammonia, we can get a black and durable writing with a comparatively small amount of silver. Take—

| | |
|---|---|
| Nitrate of silver | 15 |
| Sulphate of copper | 35 |
| Ammonia | 50 |
| Gum | 20 |
| Carbonate of soda | 20 |
| Soft water | 80 |

Dissolve the metallic salts in half the water, and add the ammonia to the solution. If the amount of ammonia above indicated does not give a clear solution, add more till the liquid is clear. The gum and soda are next dissolved in the rest of the water, hot, and the two solutions

are then mixed. This ink is of so dark a blue that no dye need be added to it. It is excellent for linen and white silk and wool. For thin fabrics the amount of gum must be somewhat increased.

It must be here remarked that when a marking ink containing gum and soda is used no preliminary preparation of the fabric is needed.

### *Silver Drawing Ink.*

For executing drawing on fabrics with silver ink, it is advisable to make the inks from special recipes, to ensure the production of the finest lines. The same recipes give excellent stamping inks, and we proceed to give a few of them.

| | |
|---|---|
| Nitrate of silver | 20 |
| Soda carbonate | 30 |
| Water | 100 |
| Tartaric acid | 7 |
| Litmus | 5 |
| Gum | 40 |

Dissolve the nitrate of silver in 40 of the water and the carbonate of soda in the remaining 60, and add the soda to the silver as long as a precipitate of carbonate of silver is formed. This white precipitate is filtered off, washed on the filter with distilled water, and rubbed up in a mortar with some water and the tartaric acid. The mass effervesces owing to the escape of carbonic acid. Ammonia is now added cautiously to dissolve the tartrate of silver, and the litmus is next added, and turns the ink blue. The gum in solution is now mixed in, and the finished ink is diluted with water if necessary. Water-soluble blue can be substituted for the litmus, the object of either being to make the writing legible from the first.

### *Red Silver Drawing Ink.*

| | |
|---|---|
| Nitrate of silver | 48 |
| Tartaric acid | 60 |
| Gum | 40 |
| Carmine | 2 |
| Water | 80 |

Rub the nitrate of silver and the tartaric acid together in a perfectly dry state and then add the ammonia to them, using no more, however, than will give perfect solution with diligent stirring. The clear solution is mixed with the gum in solution and diluted, if necessary, with water.

### *Kindt's Green Silver Ink.*

| | |
|---|---|
| Nitrate of silver | 11 |
| Ammonia | 22 |
| Carbonate of soda | 22 |
| Water | 12 |
| Gum | 50 |
| Sap green | 2 |

Dissolve the silver salt in the ammonia and the soda in the water separately. Boil the latter and pour the silver solution into it. Then add the gum, and colour with the sap green.

According to our experience the following process is better: Dissolve the silver salt in the ammonia, and add next the dry soda, and finally the sap green and the gum.

This ink only gradually blackens in the light, but the blackening can be hastened by ironing the dry writing.

### *Chloride of Silver Ink.*

A.

| | |
|---|---|
| Nitrate of silver | 8 |
| Water | 80 |
| Gum | 16 |
| Indigo-carmine | 2 |

B.

| | |
|---|---|
| Common salt | 2 |
| Gum | 5 |
| Water | 10 |

These solutions are made and kept separate. The fabric is prepared with B, and when dry is written on with A. When the writing is dry, it is exposed to the sun, and soon turns a deep black by the action of the light on the choride of silver formed from the nitrate by the common salt.

## B.—Gold Inks.

Gold, which is very easily evaporated in the metallic state from any of its compounds by organic matter, can be used with great advantage for marking inks. With it we can get at pleasure black characters, characters with a metallic lustre, or of a splendid purple colour. The markings are very difficult to efface, and it is unfortunate that the cost of such inks should be so great.

### *Black Gold Ink.*

Reade has recommended a process for preparing this ink which contains iodide of ammonium. According to his recipe, however, that salt is made in a way which entails great risk of the formation of iodide of nitrogen, which is very dangerous on account of its great explosiveness. A method of preparing the iodide which involves no such danger, however, is to saturate ammonia with sulphuretted hydrogen made by dissolving ferrous sulphide in dilute sulphuric acid. The iodine is put into the ammonium sulphide so prepared. The iodine dissolves with precipitation of sulphur, so that the liquid becomes turbid. The colourless solution of ammonium iodide is filtered off from

the precipitated sulphur, and more iodine is dissolved in it. We now dissolve gold leaf in the saturated solution, whereby we get a solution of the double iodide of gold and ammonium. If we write with this solution we get brownish-black letters, which can be made quite black by mixing the ink with one of the foregoing ammoniacal silver inks.

### *Purple Gold Ink.*

This consists of two separate liquids. A is used for the preparation of the fabric, and B for the subsequent writing.

A.

| | |
|---|---|
| Tin salt | 2 |
| Water | 200 |
| Gum | 20 |

B.

| | |
|---|---|
| Chloride of gold and sodium | 2 |
| Water | 20 |
| Gum | 2 |

Dissolve gold in strong hydrochloric acid by adding the necessary amount of nitric acid in small portions. The usual amount of nitric required is one-quarter of the weight of the hydrochloric. The impure gold solution containing copper is evaporated nearly down to dryness to get rid of the excess of acid, diluted with water, and precipitated warm with a solution of oxalic acid, which throws down a brown precipitate of metallic gold. This is washed, and again dissolved in aqua regia. Common salt is added to the solution, which on evaporation gives crystals of double chloride of gold and sodium. With this ink we write on the fabric previously prepared with solution A, whereupon Cassian purple is formed. The tint may be

made as delicate as desired by using the solutions in a sufficiently dilute state.

### *Gold Ink with Metallic Lustre.*

Here again two solutions are used, A for the preparation of the fabric, and B for the subsequent writing.

A.

| | |
|---|---|
| Oxalic acid | 2 |
| Gum | 4 |
| Water | 10 |

B.

| | |
|---|---|
| Chloride of gold and sodium | 2 |
| Gum | 4 |
| Water | 20 |

When the writing appears it is ironed and then washed.

### C.—Platinum Inks.

When platinum is dissolved in aqua regia (the above-mentioned mixtures of 4 parts hydrochloric and 1 part nitric acid) and the solution is evaporated, we get a residue of tetrachloride of platinum. If this is used alone for writing on linen we get a dead black writing, but if the fabric has been prepared with tin salt the characters will be red. As before A is the preparing, B the writing liquid.

A.

| | |
|---|---|
| Oxalic acid | 3 |
| Gum | 3 |
| Water | 10 |

B.

| | |
|---|---|
| Tetrachloride of platinum | 2 |
| Gum | 4 |
| Water | 20 |

As soon as the writing is dry and quite distinct, wash the marked place thoroughly.

## D.—Vegetable Marking Inks.

As above stated several organic bodies can be used for making marking inks, and their use is to be preferred to that of metallic salts, as the inks are not only cheaper but are, under certain conditions, more durable. Writings executed with gold, platinum, or silver salts can be gradually entirely effaced by careful treatment with cyanide of potassium or dilute acid.

It would be very easy to get any colour on a fabric with organic matter. All that is required is to mordant the fabric with alumina or tin salt, and then to write on it with a solution of the organic dye, such as cochineal, madder, logwood, etc. The result is that the characters appear in the form of a coloured lake. For fabrics which have not to be wetted this principle is taken advantage of in producing designs, and is known as textile printing, but the method does not answer for marking, as the soap and other substances used in washing clothes rapidly destroy the writing.

Of organic matters which will give an ink that will stand washing the most important are indigotine, aniline black, and the colouring matter of *Anacardium longifolium*.

## Indigotine Marking Ink.

Indigotine, the blue colouring principle of indigo, has the property of being convertible into a colourless substance called indigo-white. This substance, however, rapidly becomes indigotine again when exposed to the air, by absorbing oxygen. Indigotine will not dissolve in anything but fuming sulphuric acid.

Indigo-white is prepared from the following recipe:—

| | |
|---|---|
| Gum | 40 |
| Finest powdered dry indigo | 40 |
| Ferrous sulphate | 80 |
| Caustic soda | 80 |
| Water | 400 |
| Litmus | 2 |

Mix the indigo and the sulphate in a bottle, and then pour in the soda dissolved in the water. Cork the bottle lightly, and leave it for several days, shaking it occasionally. When all blue colour has disappeared the reaction is finished. Then place the gum and litmus in another bottle, in the state of very fine powder, and rapidly pour the indigo white upon them, and then cork the bottle immediately. When the gum has dissolved the ink is ready.

Use it by dipping a pen into the bottle and writing on the fabric, which need not be specially prepared, and cork the bottle again quickly. The writing soon turns green and finally blue, and can only be destroyed by nitric acid or chlorine. The ink in the bottle gradually forms a deposit of indigotine, which can be used for the preparation of more indigo-white.

### Anacardium Marking Ink.

There are two sorts of cashew-nuts on the market, one from the Asiatic tree *Anacardium longifolium*, the other from the American *Anacardium occidentale*. The fruits of *A. longifolium* are heart-shaped, flat, and grey or black in colour; those of *A. occidentale* are oval, greyish-green, and very lustrous. The colouring matter of both is partly of the nature of an essential oil, partly of a resin. It can be extracted from the crushed nuts with alcohol and ether,

but better by means of petroleum ether, by shaking in a well-stoppered bottle. The solution is finally filtered into a dish, where it is allowed to evaporate spontaneously to a syrup, under a sheet of paper so that no dust can get in. The resulting extract is thick enough to be used with a pen or a rubber stamp without any gum. The letters are at first brown, but are quickly changed to a deep black by alkalies. To fix and fully bring out the colour the place marked should be held for a short time over the surface of some ammonia, the alkaline fumes from which rapidly produce the desired result. The writing will then resist washing even when chloride of lime is used, and also dilute nitric acid.

### Black Copper Marking Ink.

Completely precipitate a solution of chloride of copper with one of caustic potash. Pour off the supernatant liquid and dissolve the precipitate in the smallest possible quantity of ammonia. Then add enough dextrine to enable characters which will not run to be written with a quill. When the writing is dry iron it and it will turn black.

### Aniline Marking Ink.

Aniline black makes a most excellent marking ink. The use of other anilines for marking purposes, although beautiful colours are obtained, is unadvisable, on account of the want of permanence displayed in the majority of cases by the writing. The coloured aniline marking inks are especially loose to alkali, the very agent with which they are brought into contact in the laundry. We proceed to give the best of the known recipes for aniline marking inks.

### Copper Aniline Marking Ink.

This consists of two solutions which are not mixed until just before use.

A.

| | |
|---|---|
| Chloride of copper | 15 |
| Sal ammoniac | 10 |
| Chlorate of soda | 20 |
| Water | 100 |

B.

| | |
|---|---|
| Hydrochloride of aniline | 25 |
| Gum | 20 |
| Glycerine | 5 |
| Water | 50 |

For use a small quantity of A is mixed with five times its weight of B. The result is a green liquid which turns black in a short time, and is then unfit for use. As it is, the ink has to be fixed on the dried fabric, at once, by holding it over boiling water till it is thoroughly soaked. No washing with soap will then efface the writing, which even resists chloride of lime for a long time.

### Jacobson's Marking Ink.

This also consists of two liquids, which are mixed just before use, A being added to four times its weight of B.

A.

| | |
|---|---|
| Crystallised copper chloride | 85 |
| Chlorate of sodium | 106 |
| Sal ammoniac | 53 |
| Distilled water | 600 |

B.

| | |
|---|---|
| Glycerine | 30 |
| Gum | 20 |
| Dissolved in water | 40 |
| Hydrochloride of aniline | 60 |
| Dissolved in water | 90 |

The ink is green at first, but the writing soon turns to a black which is fast to washing. This ink is known as Jetotine.

### Aniline Stamp Ink.

This again is a two-fluid ink. For use B is mixed with four times its weight of A. The writing must be fixed by leaving a hot iron on it for a few minutes.

A.

| | |
|---|---|
| Chloride of copper | 2 |
| Ammonia | 80 |
| Common salt | 2 |

B.

| | |
|---|---|
| Hydrochloride of aniline | 40 |
| Gum | 15 |
| Glycerine | 15 |
| Water | 30 |

### Black Aniline Marking Ink.

| | | |
|---|---|---|
| Aniline black | 1·75 | grammes |
| 95 per cent. spirit | 42·0 | ,, |
| Hydrochloric acid | 60 | drops |
| Gum-arabic | 2·5 | grammes |
| Water | 170·0 | ,, |

The aniline is first rubbed up with the spirit and the acid. The gum is then rubbed in after being dissolved in the water. The result is an intensely black ink, which, however, is easily washed out. In order to be able to use it for marking washing we must substitute 2·5 grammes of shellac dissolved in 170 of spirit for the gum solution.

This ink can also be used for writing on wood, glass, metal, leather, and india-rubber, and is unaffected by water.

Since the discovery of the vegetable marking inks the

demand for the much more expensive metallic marking inks has been greatly reduced, but the latter still deserve the preference so far as resistance to the alkalies used in washing is concerned. To these they are absolutely unsusceptible, so that the writing can never disappear. They can, however, be completely effaced by solution of cyanide of potassium, and writing done with silver inks can be destroyed with very dilute nitric acid. Gold and platinum can only be effaced by solutions which contain free chlorine.

A writing which is absolutely indelible can be got by writing on the fabric with a fine glass point wetted with concentrated sulphuric acid. The instant the writing turns brown, the marked place is thoroughly rinsed. In this way a part of the fibre is carbonised, and a permanent marking is secured. This method requires a good deal of practice, as the fabric is easily eaten into holes by unskilful treatment.

## XXX.

## INK SPECIALITIES.

Certain industries require particular liquids for writing on metal, leather, wood, ivory, and other materials requiring inks varying in properties.

### Ink for Metal.

#### Lustrous Black Ink for Metal.

| | |
|---|---|
| Copal | 10 |
| Oil of turpentine | 12 |
| Soot | 2 |

The copal is fused in an iron pot, and then further heated till dense fumes come off, and the copal begins to

decompose. Keep the cover of the pot handy, in case the copal should catch fire. When the copal has wasted down to about four-fifths of its original weight let the pot cool a little and stir in the turpentine gradually, and finally the soot. Care must be taken that the pot is not too hot when the turpentine is put in or it will be thrown out again. The finished mass is thinned with more oil of turpentine, if necessary, till it can be written with. The ink must be kept in well-closed bottles as it dries up quickly.

We can write with this ink upon any metal, and the writing adheres best when the surface is quite clean and somewhat rough. It should be sand-papered and then written on.

### Lustrous Red Ink for Metal.

| | |
|---|---|
| Copal | 20 |
| Oil of turpentine | 24 |
| Cinnabar | 2 |

Proceed as directed under the last recipe, except that less turpentine must be used, as the ink must be kept thick enough to prevent the cinnabar, which is very heavy, from settling.

### Lustrous Coloured Inks for Metals.

By substituting other pigments, such as ultramarine, Prussian blue, chrome-yellow, aniline violet, etc., for the cinnabar in the last recipe, ink of any desired colour may be made.

### Dull Black Ink for Metals.

| | |
|---|---|
| Copper sulphate | 10 |
| Vinegar | 2 |
| Gum | 4 |
| Soot | 2 |
| Water | 10 |

Fine dead black writing can be done on clean iron, zinc, or brass with this ink, but not on copper or tin. For these two metals we use the following recipe:—

| | |
|---|---|
| Sulphate of copper | 10 |
| Hydrochloric acid | 4 |
| Sal ammoniac | 8 |
| Soot | 2 |
| Gum | 4 |
| Water | 10 |

### Ink for Writing on Silver.

Dissolve the double chloride of gold and sodium in fifteen times its weight of water. The solution writes a beautiful golden brown on silver. If this colour is to remain the silver is dipped into ammonia and rinsed. If the writing is exposed to the sun instead, the colour soon passes into black. Black writing on silver can also be executed with a solution of tetrachloride of platinum made as above directed. If we follow engraved lines on the silver with this ink, the effect known as niello is produced.

### Black Ink for Zinc.

| | |
|---|---|
| Sulphate of copper | 2 |
| Chlorate of potash | 2 |
| Water | 72 |

On using this solution with a quill the writing is at once black. When dry, rinse with water, and go over the letters with an oiled rag.

### Black Ink for Leather.

This consists of two separate fluids. The place to be written on is painted over with A, allowed to dry, and then written on with B. The ink writes a fine black, and

penetrates deeply, especially if the back of the leather is wetted before the other side is written on.

A.

| | |
|---|---|
| Galls | 20 |
| Gum | 2 |
| Water | 200 |

B.

| | |
|---|---|
| Ferrous sulphate | 4 |
| Gum | 8 |
| Indigo-carmine | 2 |
| Water | 40 |

### Black Ink for Linen, Cotton, Wool, and Silk.

The place to be marked is prepared with solution of alum, and then, when dry, with decoction of galls. It is written on with the solution marked B in the last recipe. A slight increase in the amount of indigo-carmine makes the writing more permanent.

### Waterproof Blue Ink for Glass.

| | |
|---|---|
| Bleached shellac | 10 |
| Venice turpentine | 5 |
| Oil of turpentine | 10 |
| Powdered indigo | 5 |

Dissolve the shellac and the Venice turpentine in the oil of turpentine over hot water. Then stir in the indigo.

### Laboratory Ink.

| | |
|---|---|
| Nigrosine | 10 |
| Ruby shellac | 20 |
| Borax | 30 |
| Ammonia | 15-30 |
| Water | 400 |

Boil the shellac and the borax in the water till both are dissolved. Then filter, and add the nigrosine and the ammonia. This ink resists laboratory fumes for a long time.

## Ivory Ink.

It is possible not only to write indelibly in black on ivory, but by a simple process to execute on the material very beautiful drawings in every shade from the lightest pale brown to the deepest black.

The ivory must be first prepared by soaking it in a strong solution of soap or of ammonia, and then rinsing. In the meantime we prepare a normal ink by dissolving nitrate of silver in ten times its weight of water. The solution is divided into ten equal parts. One is left as it is, the second is diluted with its own volume of water, the third with twice its own volume of water, and so on, so that the last is diluted with nine times its volume. The weaker the solution the paler it will write on the prepared ivory, ranging from a deep black to a very light grey. By judiciously using these inks very tasteful drawings can be executed on ivory, either with brush or pen. They are indelible, and may contain all the ten shades together. If the drawing is to acquire a warm brown-gold colour the ivory is laid in a 1 per cent. solution of the double chloride of gold and sodium. As soon as the desired colour has appeared, the ivory is removed, rinsed, and immediately put into a 10 per cent. solution of hyposulphite of soda.

## Ink for Writing and Drawing on Wood.

By skilful treatment pale wood may be adorned with drawings which produce the effect of inlaid work at a

distance. The first thing to be done is to prepare the wood by painting it over repeatedly with a boiling solution of gelatine and then with the following mordant:—

| | |
|---|---|
| Alum | 10 |
| Hydrochloric acid | 10 |
| Tin salt | 2 |
| Water | 50 |

This is applied several times by means of a sponge. It partly serves as a basis for the ink, and partly prevents it from smudging by ensuring its penetration. The following inks are then used, each for the colour named:—

*Black:* Anacardium ink, painted over with ammonia when dry.
*Brown:* Solution of potassium permanganate.
*Blue:* Decoction of logwood.
*Red:* Decoction of redwood or ammoniacal cochineal ink.
*Yellow:* Decoction of Persian berries, or solution of picric acid.

## XXXI.

## SYMPATHETIC INKS.

These have no particular practical value, and are simply chemical playthings.

They are inks which can be made to change, to appear, or to disappear. Some of them are one-fluid inks, and others are two-fluid inks—one fluid being used for writing, the other for developing.

### Yellow Sympathetic Inks.

#### A.

Dissolve copper in hydrochloric acid containing a little nitric, and dilute the solution till writing with it ceases to be visible. On heating the paper the letters appear, of a yellow colour, and disappear again on cooling.

### B.

Dissolve antimony in hydrochloric acid containing a little nitric, and write with the solution. If the dry writing is painted over with decoction of galls the writing becomes visible, of a yellow colour.

### Sympathetic Gold Ink.

If paper is written on with a not too dilute solution of the double chloride of gold and sodium, the writing appears permanently on treatment with a 10 per cent. solution of oxalic acid. By ironing the paper a fine metallic lustre can be given to the characters.

### Red Sympathetic Ink.

This is a two-fluid ink. We write on paper with a very dilute solution of the double chloride of sodium and gold, and when the paper is dry we develop the hitherto invisible characters by sponging them over with a solution of tin salt, when Cassian purple is formed. If the paper is first prepared with tin salt the purple will appear at once. In a similar manner all two-fluid sympathetic inks can be used to produce a writing visible from the first.

### Disappearing Purple Ink.

Write with a very dilute solution of iron in aqua regia, and shut up the paper with a watch glass containing sulphocyanide of potassium and a little sulphuric acid. The writing soon becomes visible, of a blood-red colour, but if held over ammonia will disappear again completely.

### Green Sympathetic Ink.

A one-fluid ink is made of a mixture of cobaltous and nickelous nitrate. The characters are scarcely visible when

dry, but on heating they appear of a beautiful green, which disappears again on cooling. By varying the proportions of the two salts different shades of green can be obtained.

### Two-fluid Green Sympathetic Ink.

Write with a solution of chlorate of sodium, and when the writing is dry go over the paper with a sponge wet with solution of sulphate of copper. The writing will at once appear permanently, and of a lively green.

### Blue Sympathetic Ink.

Many cobalt salts form crystals which are red at ordinary temperatures, but turn to a full blue on heating. Hence any soluble cobalt salt can be used as a sympathetic ink. Those most used are the chloride and the nitrate. The characters are almost invisible at ordinary temperatures, but appear of a distinct dark blue when heated, again to disappear on cooling.

Paracelsus used the first green ink we described to draw the leaves of the trees in a landscape, the rest of the drawing being executed with ordinary pigments. The drawing had therefore the effect of a winter landscape when it was cold, and of a summer one when it was warmed.

### Ink with Cobalt Sulphocyanide.

This salt is extremely sensitive to changes of temperature. It gives a pale-red writing, which with a very small rise of temperature turns blue. Cobalt sulphocyanide is prepared by adding an alcoholic solution of potassium cyanide to a solution of cobaltous sulphate as long as any potassium sulphate precipitates. The filtrate is a solution of cobalt sulphocyanide and is evaporated at a very gentle heat. Writing with it turns blue even when laid in the palm of the hand.

### Brown Sympathetic Ink.

| | |
|---|---|
| Bromide of potassium | 2 |
| Sulphate of copper | 2 |
| Water | 40 |

The cold characters are scarcely visible, but turn brown on heating.

### Oxal-molybdic Ink.

Boil up a concentrated solution of oxalic acid, and add to it as much molybdic acid as it will dissolve. Preserve the solution in black bottles. The characters written with it are at first invisible, but exposed to the sun they turn dark blue, and, when heated, black.

## XXXII.

## STAMPING INKS.

These are made in various colours, and their manufacture has become an important branch of our industry since the introduction of self-inking stamps.

A good stamping ink must give a clean impression, and must not dry quickly on the stamp, so as to fill the engraving on it and make the impression indistinct. This is of especial importance with india-rubber stamps, as such stamps cannot be cleaned with a brush, which would destroy the sharp outlines of the letters and make the stamp useless.

Ordinary printers' ink has been much recommended as a stamping ink, and is most excellent for the purpose, except for one thing. It gives a sharp, black impression which dries very quickly on the object stamped, but the ink

dries almost as fast on the stamp. This may be remedied, however, by dilution with one-tenth to one-sixth of its volume of filtered linseed oil. Too much of the oil must, however, not be added, for it will not only make the ink too thin and pale, but will cause the impression to be surrounded with a transparent, greasy border.

### Black Stamping Ink.

| | |
|---|---|
| Finest lampblack | 10 |
| Gum | 4 |
| Glycerine | 4 |
| Water | 3 |

Dissolve the gum in the water, add the glycerine, and rub the mixture up intimately with the lampblack. The glycerine, which is thick but not greasy, absorbs moisture from the air, and so keeps the ink liquid. For very minutely engraved stamps the proportion of black is increased, to make the ink rather thicker. This excellent ink will not run, and gives very sharp impressions.

### Coloured Stamping Inks.

These are obtained by replacing the lampblack in the last recipe by other pigments, according to the colour desired, such as chrome-yellow, red lead, ochre, green cinnabar, green ultramarine, indigo, ultramarine, Prussian blue, red ochre, umber, etc.

### Aniline Stamping Inks.

Very beautiful stamping inks can be made with the coal-tar colours, but some skill is required in doing so. The manufacture is simple enough if the dyes are used in the solid form, for they have merely to be rubbed up to a uniform mass with glycerine and mucilage. If, how-

ever, they are to be used in solution, it must be a concentrated solution in the strongest spirit. To this solution glycerine is first added, and the gum is put last, and very gradually. It is also a good plan to replace from a quarter to a third of the gum by sugar.

### Soluble Stamping Inks.

Since the discovery of aniline dyes soluble in water the manufacture of excellent stamping inks has become very simple with their aid. The best to use is water-soluble blue. This is made into a syrup with glycerine. This syrup is applied with a brush to a smooth, soft pad, and rubbed in uniformly with a wooden spatula. A single application to a small pad of about 8 square inches area is enough to enable a rubber stamp to produce hundreds of impressions. The composition of the ink depends on whether it is to be placed on a pad or is to be filled into a soft inking stamp. In the first case it must be thick, so that enough may adhere to the stamp to give a good impression. In the latter case, where the ink has to pass through a filter to the stamp from a reservoir, it must be more fluid, so that it will pass through fast enough to allow the stamp to be quickly used many times.

### Indelible Stamping Ink.

Many textile manufacturers desire to so mark their goods that they can be washed, bleached, and dyed without affecting the marking.

One body only is known which resists all chemical reagents entirely, namely carbon. Hence an indelible stamping ink must contain that pigment. The best is ordinary printing ink diluted with one-quarter of its volume of good boiled linseed oil, which makes it penetrate deeply into the

fabric and become absolutely indelible. All known bleaching agents leave it quite unchanged. It can, it is true, be hidden by dyeing the fabric, but then if the dye is destroyed with chlorine water or very dilute aqua regia the marking shows up with perfect distinctness.

## XXXIII.

## LAUNDRY OR WASHING BLUE.

It is well known that the last rinsing water is mixed with a little blue to neutralise the yellow tinge of the linen and make it a pure white. Many blues are put on the market for this purpose, such as smalts, Prussian blue, sulphindigotic acid and indigo-carmine, both in a solid state and as solutions.

It is easy to see that solutions of colouring matter are preferable to solid powders, as they can reach the interior of the fibre, while the powders can only adhere mechanically to the outer surface.

### A.—Insoluble Laundry Blue.

#### *Smalts.*

Smalts or eschel is a blue glass. It is made by fusing cobalt ores with carbonate of potash and quartz. The glass is ground and levigated with the greatest care. Smalts is thus obtained in several different degrees of fineness and shade of colour.

When smalts is used as a laundry blue it must be carefully mixed uniformly with the starch, which makes it adhere to the garment. There is a powdered washing blue on the market which is an intimate mixture of smalts and starch. When boiled with water it is used in the laundry.

### *Prussian Blue.*

This has already been spoken of several times in this book. It is dark blue with a coppery shade, and the darker sorts are called Paris blue.

If we make our own Prussian blue and leave the wet precipitate for some hours in strong nitric acid, we shall get a product equal to the best Paris blue.

Prussian blue, like smalts, can only be used in combination with starch or gum. It is a very intense colour, so that care must be taken that it does not make the linen look blue instead of white.

A great drawback to the use of Prussian blue as a washing blue consists in the fact that linen on which it has been frequently used gradually assumes a yellow tinge, owing to the action of the washing soda and soap in the Prussian blue and the slow formation of brownish-yellow oxide of iron on the fabric.

## B.—Soluble Laundry Blue.

### *Soluble Prussian Blue.*

This is prepared for laundry purposes exactly as for ink making. It can be poured into the water in which the linen is rinsed, and need not be mixed with starch or gum.

Although the soluble Prussian blue has the same drawback as that just mentioned as attaching to the ordinary pigment, it has it to a much smaller extent, as the oxalic acid in which the blue is dissolved has also a solvent action on the oxide of iron.

It may here be mentioned that iron-moulded linen can be made perfectly white again by twenty-four hours' immersion in a one-tenth per cent. solution of oxalic acid in distilled water.

### *Indigo Laundry Blue.*

These are the most to be recommended of all washing blues, as they injure the washing in no way, are all freely soluble in water, and adhere very uniformly to the linen. They are used either as sulphindigotic acid, which is only employed in solution, or as indigo-carmine, which may be used as a powder, as a paste, or in solution.

### *Sulphindigotic Acid.*

This is easily made by thoroughly drying powdered indigo, and then stirring it up with twice its weight of fuming sulphuric acid. The mass, which gets very hot, is well stirred with a stout glass rod, and then left to stand for twelve hours. The whole is then put into a funnel plugged with asbestos. The solution of sulphindigotic then drains through. It will be so strong as to look quite black. The insoluble residue on the filter should be rinsed with water, and the rinsings allowed to mingle with the rest of the filtrate. The washed residue is again dried, and serves for the production of more sulphindigotic acid with a fresh lot of ingredients. It is of great importance that the indigo should in each operation be in excess of the sulphuric acid, so that none of that acid can be present in the solution of the sulphindigotic acid. Such an excess would have a most destructive effect upon the garments. The solution of sulphindigotic acid may be bought concentrated under the name of indigo washing blue essence, or diluted, as indigo washing blue. A few drops of the essence are sufficient for a large washing tub of water.

### *Indigo-carmine.*

The preparation of this substance has been already described. We have, therefore, only to say a few words about the various forms in which it comes upon the market.

The paste form, although highly concentrated, is not favoured by the laundry trade, as it is so difficult to avoid taking too much of it, and so making the linen blue. The solution is sold in different degrees of concentration, as indigo-carmine essence and indigo-carmine washing blue. The essence is made by adding to the paste just enough water to make a solution. It looks quite black, except in very thin layers indeed.

### *Solid Indigo-carmine.*

We have succeeded in producing a preparation which is an excellent washing blue, and consists of solid indigo-carmine. We make the carmine into a thick paste with potato starch. This, when perfectly uniform, is moulded into cakes in the form in which water colours are usually sold. The cakes are got out from the moulds by tapping the back, and are dried until they are quite hard, have a shining surface, and do not soil dry fingers. It is best to dry them on the water-bath, which obviates the possibility of overheating. When a cake is boiled in water a starch paste is got in which the indigo-carmine is suspended in the finest subdivision. This paste can be mixed uniformly with more water for bluing the linen.

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